AN ABSTRACT OF THE DISSERTATION OF

<u>Stephen T. Meyers</u> for the degree of <u>Doctor of Philosophy</u> in <u>Chemistry</u> presented on <u>August 28, 2008</u>. Title: Aqueous Chemistries for Oxide Electronics

Abstract approved: _____

Douglas A. Keszler

The variegated aqueous chemistries of metal cations are applied to the design and synthesis of non-toxic solution precursors suitable for additive printing of large-area Polycondensation behaviors of aqueous Al^{+3} and PO_4^{+3} are oxide electronics. manipulated in the deposition of atomically smooth amorphous aluminum oxide phosphate (AIPO) dielectric films. AIPO gate dielectrics with performance parameters not previously demonstrated via solution are integrated in thin-film transistors (TFTs). Simple zinc-ammine coordination chemistries enable low-temperature ink-jet printing of ZnO semiconductor films. Solution deposited ZnO films processed at low temperatures are integrated with AIPO dielectrics in high-performance TFTs. Discrete group 13 heterometallic hydroxo clusters are developed as aqueous precursors for InGaO₃ semiconductor films. Insights from these polynuclear clusters are utilized in the synthesis of aqueous precursors for amorphous InGaZnO₄ semiconductor films. These channels are similarly integrated with solution processed AlPO dielectrics on glass substrates, thereby demonstrating the potential for solution processed oxide macroelectronics.

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by Stephen T. Meyers

A DISSERTATION

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APPROVED:

Major Professor, representing Chemistry

Chair of the Department of Chemistry

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Stephen T. Meyers, Author

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Aqueous Inks for Oxide Electronics

Chapter 1

INTRODUCTION TO MACROELECTRONICS AND SOLUTION PROCESSED OXIDE THIN FILMS

Introduction to Macroelectronics

The advent of the silicon integrated circuit and the subsequent advances in microelectronics over the past half-century have driven exponential increases in computational densities and a simultaneous decrease in manufacturing costs. The miniaturization of Si complementary metal-oxide-semiconductor (CMOS) technology has proven revolutionary, yet a wide and varied class of devices can not be improved by decreasing size, and indeed may require large-area integrated electronics. These macroelectronic devices, exemplified by active matrix flat panel displays (FPDs), cannot be manufactured economically using CMOS microtechnology. Instead, the march of the FPD to cell-phone ubiquity and wall-covering dimensions has been enabled by adapting the materials (amorphous silicon, or α -Si) and methodologies (photolithography) of microelectronics to macro applications. Combined with appropriate economies of scale, these adaptations have been hugely successful; global FPD sales were projected to exceed \$120 billion dollars in 2008.¹ However, as with any technology, maturation has exposed limitations in both future cost reductions and capabilities for α -Si based macroelectronics. The subject of this dissertation is a series of chemical investigations into one potential successor technology: solution-processed oxide electronics.

To set the stage for these investigations a short introduction to the fundamental building block of active macroelectronics, the thin-film transistor (TFT) is useful, as in later chapters these devices will form the primary test vehicles for the functional demonstration of both solution-processed oxide semiconductors and insulators. This will be followed by a brief overview of the incumbent amorphous silicon (α -Si) TFT technology, and an outline of its limitations with respect to future macroelectronic applications. Solution processed oxide electronics are then introduced as a potential successor technology. The solid state chemistry and physics of oxide materials are therefore discussed as it relates to TFT operation. Finally, a unifying description of the aqueous deposition chemistries proposed in this work is provided.

Thin-Film Transistors

Materials chemistry is by nature application oriented; chemical principles are applied in the design and synthesis of materials and chemistries to provide a given function. Testing this functionality usually involves some physics and engineering principles not familiar to the chemist. In the case of solution-processed oxide semiconductors and dielectrics, ultimate functionality is tested by integration in field-effect thin-film transistors. Such devices form one of the primary components of macroelectronics by providing active control over passive components such as capacitors, light emitting diodes, or sensors. An in-depth, quantitative theoretical treatment of the fundamentals of TFT operation, as well as some of the commonly encountered non-idealities is given by Greve² and Wager.³ A simple qualitative understanding of the device as a three terminal extension of a metal-insulator-semiconductor MIS capacitor is useful for the chemist without a device physics or engineering background.

Field-effect TFTs are simple switches where the flow of current between two terminals (the Source and Drain) in a thin (< 500 nm) semiconductor layer is controlled by a voltage applied to a third terminal (Gate) isolated from the semiconductor by an insulating layer as depicted in Figure 1.1a. Consideration of a band diagram at the Metal-Insulator-Semiconductor interfaces forms the picture of the MIS capacitor shown in figure 1.2a. The n-type channel is considered to be a disordered semiconductor with a non-zero density of localized mid-gap states. At equilibrium those states below the Fermi level (E_F) are assumed to be filled donor states, while those above are considered as empty acceptor states. When a small positive voltage is applied to the gate electrode the bands bend at the insulatorsemiconductor interface, and the positive charge on the gate is balanced as electrons fill the localized acceptor states (Q_T) ; the conduction band (E_C) remains largely empty (Figure 1.2b). With increasing positive bias on the gate, localized acceptor states are filled, and eventually the mobile charge (Q_m) in the conduction band begins to increase (Figure 1.2c). This MIS capacitor can be placed in the context of the TFT structure in Figure 1.1a when a small, positive bias is applied to the drain electrode (V_{DS}) . In the absence of applied gate bias $(V_{GS} = 0)$ no current flows; because there is not a significant population of mobile electrons in the channel conduction band the drain-source current (I_D) nominally zero. When V_{GS} is increased to a critical value, (V_{on}) itinerant electrons begin to accumulate in the channel, I_D sharply increases, and the device turns "on." This effect is illustrated in a logarithmic plot of I_D versus V_{GS} in Figure 1.3a. Note that the "off" current when $V_{GS} < V_{on}$ is not actually zero due to a

combination of gate leakage (I_{GS}), a non-zero equilibrium carrier concentration in the conduction band, non-zero conduction between donor states, and instrumental noise. The precise value of V_{on} is determined by many factors, including the trap density and equilibrium carrier concentration in the semiconductor, as well as the capacitance density of the insulator and any trapped charge at the interface. Because it determines the switching voltage of the device it is one of the primary material/device parameters.

While I_D is "switched" on and off via V_{GS} , the magnitude of I_D when $V_{GS} > V_{on}$ is also determined by the drain-source voltage (V_{DS}). At a constant V_{GS} (> V_{on}) I_D increases linearly with V_{DS} according to Ohm's Law until $V_{DS} = V_{GS} - V_{ON}$. At this point I_D saturates, and remains constant with increasing V_{DS} , as shown in the plot of I_D vs. V_{DS} in Figure 1.3b. The cause of this behavior is illustrated in Figure 1.1b and c. At low V_{DS} values the layer of accumulated charge at the semiconductor-dielectric interface formed by the potential on this effective MIS capacitor is largely uniform. However, as V_{DS} approaches $V_{GS} - V_{ON}$ the electric field creating the accumulation layer decreases near the drain, and finally reaches zero, effectively "pinching-off" the channel, and leading to current saturation. By approximating the induced mobile charge in the accumulation layer and integrating over the channel potential two expressions to model I_D are developed via square-law theory. The first is valid in the linear regime where while the second is valid for the saturation regime.

$$I_{DLIN} = \frac{W}{L} C_G \mu \left[(V_{GS} - V_{ON}) V_{DS} - \frac{V_{DS}^2}{2} \right], \quad (V_{DS} < V_{GS} - V_{ON})$$
(1.1)

$$I_{DSAT} = \frac{W}{2L} C_G \mu (V_{GS} - V_{ON})^2, \quad (V_{DS} \ge V_{GS} - V_{ON})$$
(1.2)

In both cases I_D is directly proportional to C_G , the gate capacitance, and μ , the semiconductor channel device mobility. (*W/L* is a geometric factor equal to the width to length ratio of the device).

TFT Channel Mobility

Considering the principal function of a TFT is as a high-dynamic-range switch, the most important device parameters are the switching voltage (V_{on}) and the I_D on-to-off current ratio (I_{on}/I_{off}). From Equation 1.2 it is clear that to boost the latter parameter (in the form of maximal I_{DSAT}) both the gate dielectric (C_G) and semiconductor (μ) must be optimized. In this context the properties of an ideal gate dielectric are discussed in Chapter 2, while a short review of semiconductor device mobility is undertaken below.

The literature on semiconductor research for TFT applications is often dominated by reported mobility values, yet the contextual meaning of such values is often misunderstood or misrepresented. Part of this confusion may be attributed to the deceptive simplicity of equation 1.2. Provided an I_{DSAT} value can be obtained, no matter how qualitatively poor the device operation, solving this equation will provide a value (identified as μ_{SAT}), which is often stated without regard to its meaning. In short, unless the other, primary parameters such as V_{on} , I_{on}/I_{off} , and I_g are within a suitable range for the desired application, any extracted mobility is practically meaningless. Even in qualitatively ideal TFTs, it is often overlooked that the extracted value is fundamentally a *device* parameter—measuring a net mobility of carriers in an

accumulated channel at the semiconductor-dielectric interface under an applied field with only minimal relation to a bulk semiconductor property. In fact, μ_{SAT} is itself only a rough estimate of a slightly more precise approximation as it neglects the influence of gate voltage on mobility, an important consideration given the nonnegligible density of trap states in disordered semiconductors. For device mobilities quoted in this paper, the methods of Hoffman⁴ and Hong⁵ have been followed in the extraction of an incremental mobility, μ_{inc} which is meaningful only when accompanied by the V_{GS} value at extraction. Their derivation is made in the linear regime of TFT operation ($V_{DS} \ll V_{GS} - V_{ON}$) where the channel charge is largely uniform, and carrier drift is dominant. The result is

$$\mu_{inc} = \frac{\frac{\partial g_d}{\partial V_{GS}}}{\frac{W}{L}C_G}$$
(1.3)

where g_d is the small-signal drain conductance (estimated from discrete large-signal data points in $I_D - V_{DS}$ measurements)

$$g_{d} = \frac{\partial I_{D}}{\partial V_{DS}} \bigg|_{V_{GS} = \text{Constant}}$$
(1.4)

A plot of μ_{inc} as a function of V_{GS} is shown in Figure 1.3c. The strong dependence of μ_{inc} on gate voltage is notable, and consistent with a physical interpretation of μ_{inc} as the mobility of new charge carriers added to the channel by an incremental increase in gate voltage. This is an important effect of the disorder native to thin-film semiconductors. Initial carriers accumulated in the channel have low mobility, either

due to formation of energy barriers at grain boundaries via charge trapping in a polycrystalline material,⁶ or because of a non-zero density of band-tail states extending into the energy gap in an amorphous film.² In both cases, as V_{GS} increases the Fermi level pushes near or into conduction band, decreasing the barrier height or filling traps, thereby increasing mobility for newly induced carriers.

Amorphous Silicon Technology

The birth of macroelectronics in its two most visible forms—active matrix display and thin-film photovoltaics—can be traced to the demonstration of bipolar carrier control and field-effect in amorphous silicon (α -Si) in the late 1970s.^{7,8} TFTs with hydrogenated α -Si (α -Si:H) semiconductor channels remain the primary pixel switch elements in most active matrix displays today. While α -Si:H composition and optoelectronic properties vary widely with H content and deposition conditions, the material may be generally considered as a random network of Si atoms covalently bonded via sp^3 hybridized orbitals with bond angles clustered about the 109.5° characteristic of an ideal tetrahedron. Hydrogenation serves to "passivate" electrically active dangling bonds left by incomplete tetraheda in the network. α -Si:H has attained prominence by offering reproducibly high on-to-off current ratios and moderate TFT switching voltages relative to competing Cd-chalcogenide technologies developed at the same time.²

The disordered nature of α -Si:H is key to low cost, large-area deposition relative to expensive single crystal silicon, though a stiff performance penalty accompanies this

disorder. The highly directional sp^3 bond network in Si is extremely sensitive to bondangle distortions, which prevent electron dispersion and true band conduction. As perfect tetrahedra are impossible in the amorphous phase, electron device mobility in α -Si:H ($\leq 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is reduced by 2-3 orders of magnitude relative to the crystalline phase. Moreover, even with hydrogenation, the numerous photo and electrically active defects associated with unsatisfied bonds combine with localized trap states to limit device stability. Thus while suitable for relatively low-speed voltage-driven applications (e.g pixel capacitor switches) this modest mobility and stability limits the usefulness of α -Si in other macroelectronic applications where switching speed and low power current drive are important.

The adaptation of Si in a disordered form for macroelectronics is mirrored in a similar adaptation of microelectronic manufacturing techniques, notably photolithography. Most thin-film layers are deposited via vacuum methods, usually dc-sputtering or CVD. This deposition itself is a difficult and expensive process when nanometer thickness uniformity is required over multiple square meters. This daunting economic picture is compounded by the need to subtractively pattern each layer to a 1-10 µm resolution. The photolithographic procedures used for feature definition consist of photoresist coating, baking, exposure, development, etch and cleaning steps. Most TFT-LCD process flows require repeating these photo-patterning steps for up to five different masks. FPD manufacturing costs have therefore been driven down in part by the use of ever-larger glass substrates on which photo patterns are stepped to create "smaller" (up to 1.5 m diag) devices. However, the economic

benefit of ever-larger substrates has continued to diminish given the equipment costs and process difficulties associated with huge glass panels. (10^{th} generation glass = 2.85 x 3.05 m). Considering the stagnating manufacturing costs associated with vacuum deposition and subtractive patterning relative to the performance limitations of α -Si:H, a consensus has emerged that new technologies will be required to propel future macroelectronic cost reductions and enable new applications.

Additive Solution Processing

On the cost front, a primary candidate, and unifying theme of this dissertation, is the use of additive liquid phase printing techniques to deposit and pattern the active array in a single step. Because the feature size for most macroelectronic devices is relatively large (>1 μ m), numerous printing strategies including inkjet,^{9,10} gravure,¹¹ microcontact,¹² and screen printing,¹³ as well as mist deposition have the potential to eliminate costly and wasteful photolithography steps, and large, expensive vacuum deposition tools. The relative advantages of these techniques have been reviewed elsewhere,^{14,15} and indeed, are largely moot until the development of suitable precursor chemistries, as specific modifications to each will be required to take advantage of high-performance precursors.

As precursor "ink" development is chemical in nature, the two solution deposition techniques used in these investigations demonstrate simple chemical functionality of the ink. The first, and most common technique, is spin coating. In this process an excess of the precursor solution is deposited on a substrate, after which the substrate is rotated at high rpm (> 1000). Centrifugal force causes the liquid to flow radially outward, thinning and expelling excess solution from the perimeter of the substrate in the form of droplets. Evaporation of the solvent and thinning of the liquid film increases its flow resistance, eventually ending radial flow, while the film continues to thin via evaporation. When the film has reached an approximately constant thickness an energetic (thermal, light, etc.) curing step is generally used to remove additional solvent and polymerize the film prior to additional coating or processing. The precise thickness and properties of the resulting film are dependent upon spin-speed, solution viscosity, solvent vapor pressure, and surface tension.^{16,17} However, relative to more complex deposition systems the simplicity and chemical compatibility of spin coating is high, making it an excellent development technique.

While simple, and useful for large-area deposition of uniform films, spin-coating is not additive in nature. Thermal ink-jet (TIJ) printing does offer direct patterning capability, and significant research into this area has allowed self-aligned features <100 nm.¹⁸ Modified TIJ printers are used in Chapter 4 to deposit ZnO channels, and in this case the process used has a direct impact on precursor chemistry. In Figure 1.4 a schematic of a basic TIJ architecture is shown. Each print head consists of a firing chamber with a resistive heater, an orifice layer and nozzle, and an ink feed system. To deposit a drop of solution a current pulse is applied to the heater, which vaporizes a thin layer of solution near the resistor. The resulting gas bubble expands rapidly, over coming the surface tension of ink at the nozzle and expelling a drop of ink. As with all solution deposition techniques patterning and film formation are highly dependent

on ink properties relative to the geometry and materials of the deposition system.^{15,19,20} In particular the surface energy relative to the orifice layer and viscosity of the ink must be sufficient to prevent leakage, but not too high to prevent expulsion of the drop. Finally, because a small portion of the ink is vaporized, non-volatile species may condense either on the resistor surface, or in the bulk ink itself, thereby clogging the head or disabling the resistive heater.

Oxide Semiconductors

Mass adoption of solution deposition for active macroelectronics is predicated on a coincident cost *and* performance improvement over α -Si. As described above, the primary determinants of TFT performance are the semiconductor and insulating layers. Although a number of materials systems and solution chemistries have been proposed to meet this simultaneous requirement (see Chapter 4), metal oxides are among the most promising from both solid-state and solution chemistry perspectives. A low-leakage, high-permittivity gate dielectric is arguably the more difficult target, and for this application, oxides, epitomized by thermally-grown SiO₂, are well established, although largely unproven via solution. The physics and chemistry of oxide dielectrics are covered in Chapter 2. High-mobility oxide semiconductors with easily modulated carrier densities are a more recent phenomenon; the solid state physics and chemistry of these materials are here reviewed as they relate to device functionality and amenability to solution processing.

If high-performance oxide-semiconductor TFTs are a recent advance, the materials themselves have an extensive history. Conductive oxides comprising degenerate n-type polycrystalline In₂O₃, SnO₂, and ZnO have been in widespread use since the 1940s.²¹ Moreover, the earliest reported polycrystalline oxide-channel TFTs pre-date α -Si by more than a decade, although the limited characterization of these TFTs suggests relatively poor modulation of free carrier density and mobility.^{22,23} The shift of attention to more controllable α -Si limited research on the TFT-channel properties of these oxides until the late 1990s, whereupon an interest in transparent electronics begat an oxide semiconductor renaissance.

Optical transparency may enable new applications, but is here considered an ancillary benefit. The electronic structure imparting this large band-gap is, however, crucial to high performance TFT channels (for a more complete treatment see Woodward,²⁴ Wager,³ Cox,²⁵ and Duffy²⁶). Of the many oxides demonstrating semiconducting properties under appropriate conditions, it is no coincidence that the highest conductivities and carrier mobilities have been observed in the In₂O₃, SnO₂, and ZnO systems (similar properties are accessible in CdO, although the toxicity of Cd limits its realistic macroelectronic utility). Despite disparate crystal structures, these polar-covalent oxides share a cation $(n-1)d^{10}ns^0$ electron configuration (where n > 4), while the oxide anion adopts the expected $2s^22p^6$ configuration. As anticipated from a simple ionic model, the Valence Band (VB) is associated primarily with the filled O 2p orbitals, while the Conduction Band (CB) is primarily metal *ns* in character. The symmetry-associated nuances of band theory do not appreciably alter this picture,

though it is relevant to note that while the energy of isolated M *ns* and O 2*p* orbitals are sufficiently similar to allow overlap, symmetry conditions at the Γ point limit antibonding M *ns*–O 2*p* overlap, preserving the M *ns* character of the bottom edge of the conduction band. Moving off the Γ point relaxes this condition and the increasing O 2*p* overlap drives up the band energy; hence the large dispersion/bandwidth and high bulk electron mobilities (for electrovalent compounds) observed for these oxides.²⁴

Consistent with optical transparency, the magnitude of the energy gaps (E_g) for In₂O₃, SnO₂, and ZnO are all > 3.4 eV. In a stoichiometric sample the Fermi level would lie near the middle of the energy gap, but in practice a significant concentration of intrinsic oxygen-deficient defects place the Fermi 1 evel near the CB minimum making most samples inherently n-type. The precise nature of these defects is neither clear nor consistent among the p-block oxides in question, but the demonstration of carrier control via oxygen partial pressure in vacuum deposited films is both compelling evidence, and a crucial part of TFT channel development. Extrinsic n-type doping is also possible, generally on the cation site, (e.g. Al⁺³ in ZnO, or Sn⁺⁴ in In₂O₃) and occasionally on the anion site (F⁻). P-type acceptor doping in these oxides is difficult due to the spontaneous formation of intrinsic compensation defects which tend to "pin" the Fermi level well above the VB.^{27,28} Moreover, the relatively flat O 2*p* dominated VB ensures a low hole mobility. Nonetheless, p-type ZnO in particular remains an active, if elusive research topic.

Thus far we have only considered polycrystalline oxides. From a macroelectronic perspective, these films appear viable, as in contrast to polycrystalline Si, the activation energy for crystallization for these materials is generally low, so that most vacuum deposition methods are energetic enough to produce a nanocrystalline film without further processing. The solid-state benefit of oxides here is primarily in the low-temperature crystallization and the ability to vary intrinsic doping levels over a wide range. Carrier mobility in a polycrystalline film is principally determined by grain boundary (GB) scattering, therefore optimization of carrier concentrations and thus GB barrier height can lead to relatively high device mobilities.²⁹ Despite this performance potential, nanocrystalline oxide semiconductors pose serious TFT integration problems. The largest is associated with facile GB diffusion, which allows adsorption and desorption of charge-trapping gas molecules under various environmental and bias conditions, altering device performance. Even with passivation the net result is that device performance is highly process dependent, to the extent that a wide range of nanocrystalline ZnO behavior has been reported under nominally identical processing conditions.

In this light, the advantages of an amorphous oxide semiconductor (AOS) are significant. The diffuse, isotropic nature of the M *ns* orbitals comprising the CB minimum results in orbital overlap and bandwidth that is largely insensitive to the coordination environment around the cation. The net effect is that AOSs comprised of these binary components maintain Hall and device mobilities similar to the single crystal material, in direct contrast to α -Si. Another important feature is that free

carrier density remains controllable in the form of oxygen non-stoichiometries. Indeed, it is possible to increase carrier density from insulating to degenerate levels under appropriate deposition and processing conditions. Several amorphous systems of this type have been demonstrated, including $ZnO-In_2O_3$ (ZIO),³⁰ $ZnO-SnO_2$ (ZTO),³¹ CdO-GeO₂,³² In_2O_3 -Ga₂O₃ (IGO),³³ and In_2O_3 -Ga₂O₃-ZnO (IGZO).³⁴ The last system has attracted the most study, achieving thin-film hall mobilities ~10 cm² V⁻¹ s⁻¹ only, slightly less than that observed in epitaxial single crystal films.³⁵

The ideal carrier concentration for an n-channel oxide semiconductor completely fills the localized states native to the disordered film, meaning that additional carriers accumulated with increasing V_{GS} are mobile, and device V_{on} is near zero. The intrinsic or extrinsic doping level required to meet this condition is therefore dependent on the trap density in the film. An excessive carrier concentration results in equilibrium band conduction and a channel layer that is normally "on."

Aqueous Chemistries for Oxide Electronics

If the foregoing discussions have identified a need (cost and performance limitations of α -Si technology) and proposed a resolution (additive printing of oxide electronics) the chemical route to execution remains obscure. To some extent this is attributable to the embryonic nature of oxide TFT research, yet the following chapters review voluminous publications indicating that considerable effort has been expended towards this goal. To a first approximation, the majority of the solution chemistries in this vast body of literature appear to rely on the simple thermodynamic fact that most

forms of the metals in question will convert to an oxide when heated in air. Conversion pathways between solution and oxide film are infrequently addressed as they relate to processing temperature and chemical composition, and even more seldom in relation to the electronic structure of the target film, the ultimate arbiter of functionality.

The investigations described in the following chapters represent an attempt to tailor specific solution chemistries for optimal conversion to a given oxide film (in this case the p-block and late transition-metal oxides introduced above). The aqueous character these solutions is no accident, rather a logical consequence of the stated goal. Successful chemical solution deposition requires a minimum liquid precursor stability, formation of a liquid film, liquid evaporation, and reaction of the metal species to form a dense, low-defect oxide bond network. Practicality supplies additional constraints of speed, temperature, and scale. Given the liquid precursor stability requirement, solvation of high-charge-density metal cations in a highly polar solvent such as H₂O is almost a prerequisite, yet the true value of the aquo ligand lies in its capacity as a reactant in the formation of the oxide bond network.

The reactivity of solvated cations is well known, though the intricacies of the associated processes of hydrolysis

$$[M(OH_2)_x]^{z+} + H_2O \longrightarrow [M(OH_2)_{x-1}(OH)]^{(z-1)+} + H_3O^+$$

and condensation

$$M - OH + M - OH \longrightarrow M - OH - M, M \begin{pmatrix} OH \\ OH \end{pmatrix} M, M - O - M$$

are incompletely understood even for the most common cations.^{36,37} Indeed, aquocation reactivity with respect to precipitation of hydroxides and oxyhydroxides under pH pressure is so great that common oxide solution deposition techniques suppress these reactions with non-aqueous primary solvents, strongly binding ligands, and/or excess mineral acid or base. Thus rapid, low-energy, and low volume-loss condensation processes are hobbled to diffusion limited, high-energy, and disruptive decomposition and conversion reactions.

Balancing competing aqueous cation complex stability and reactivity is therefore a fundamental objective of this work. A variety of chemical methodologies are applied to resolve this stability/reactivity dichotomy, depending on the cations in the target oxide. In Chapters 2 and 3, hetero-polycondensation reactions between metal cations and oxo-anions are harnessed to provide stable solutions that condense under applied heat to form dense, smooth aluminum-oxide phosphate dielectric films. An exceedingly simple low-temperature reaction pathway to ZnO semiconductor films is demonstrated in Chapter 4. Purified zinc-ammine solutions are shown to decompose to the oxide near room temperature, enabling ink-jet printing of high-mobility semiconducting films. An entirely novel synthetic strategy is used to produce partially condensed heterometallic hydroxo clusters in a mixed-solvent system in Chapter 5. Transfer to an aqueous environment generates a meta-stable precursor suitable for amorphous InGaO₃ semiconductor films. Application of a similar technique in Chapter 6 allows quaternary InGaZnO₄ semiconductor thin films. In all cases chemistry is validated by functionality, as oxide films are integrated in highperformance TFT test structures. Development of a printed oxide technology platform is advanced through integration of each solution processed semiconductor with a gate dielectric likewise deposited via aqueous condensation chemistries. The exceptional performance realized in these integrated devices not only validates the aqueous chemistry chosen, but also the potential for high-performance printed oxide electronics.
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Figures



Figure 1.1 Schematic structure and operation of a bottom-gate n-channel TFT. a) When $V_{GS} > V_{on}$ there are no free carriers in the channel, I_D is nominally zero and the device is off. b) When $V_{GS} > V_{on}$ electrons are accumulated at the semiconductor insulator interface I_D increases exponentially and the device turns on. If V_{DS} is small relative to $V_{GS} - V_{on}$ the accumulation layer is assumed to be uniform across the channel and I_D increases linearly with V_{DS} . c) As V_{DS} increases and approaches $V_{GS} - V_{on}$ the accumulation layer is "pinched off," I_D saturates, and remains constant with increasing V_{DS} .



Figure 1.2 Band diagram of a thin-film MIS capacitor considered as a TFT component. a) At equilibrium localized mid gap states below E_F are filled, while the free carrier population in the conduction band is negligible. b) When a small positive V_{GS} is applied to the gate, the semiconductor bands bend at the interface. The accumulated carriers are largely trapped (Q_T) in empty mid-gap acceptor states. c) At large positive V_{GS} values ($V_{GS} > V_{on}$ in the TFT context) the accumulated charge is sufficient to fill the majority of trap states; delocalized carriers begin to populate the conduction band.



Figure 1.3 Quantitative operation of an actual device approximating the schematic TFT in Figure 1.1. a) Log $I_D - V_{GS}$ characteristics extracted in the linear regime ($V_{DS} = 1$ V). V_{on} is clearly evident, and I_{on}/I_{off} is ~ 10⁶ at 40 V_{GS} . I_G remains low even at high V_{GS} values. b) $I_D - V_{DS}$ characteristics of the same device. Despite slightly non-ideal behavior, current saturation is readily apparent as V_{DS} is increased at constant V_{GS} values. c) μ_{inc} , extracted from the data points in Figure 1.3a plotted versus V_{GS} .



Figure 1.4 Firing chamber and nozzle of a thermal inkjet print head.

Chapter 2

OXIDE DIELECTRIC FILMS FOR ACTIVE ELECTRONICS

Douglas A. Keszler, Jeremy T. Anderson, Stephen T. Meyers

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Introduction

In this chapter, we consider the solution deposition of high-quality oxide dielectric thin films for the fabrication of active electronic devices. The importance of such insulating films is readily appreciated by considering the pervasive use of integrated circuits built from Si-based CMOS devices, where utility is largely predicated on the superior insulating properties of SiO_2 as opposed to the rather modest semiconductor performance of Si.¹ While the advances in solution-processed semiconductors detailed in this volume are impressive, it is important to note that their device implementation through additive processing will generally require suitable oxide dielectric materials. But, solution-processed oxide films, because of their deposition, morphological characteristics and performance limitations, are often found to be poor mimics of vapor-deposited counterparts. Such has certainly been the case for integrated highperformance insulators, especially in the context of enabling direct methods of highspeed printing and patterning. While establishing capabilities to print and integrate high-quality oxide dielectrics poses a very significant challenge for solution processing, success is very likely to open many opportunities in fabricating active electronics, as well as providing new approaches to the production of a variety of unique optical and optoelectronic devices.

Gate Dielectric Materials Selection

The function, utility, and design parameters for an insulator in a field-effect thinfilm transistor (TFT) are conveniently exemplified by considering the bottom-gate staggered device shown in Figure 2.1. In this transistor, source-to-drain current through the semiconductor (channel) is modulated by a field imposed on the semiconductor via the metal-insulator gate.

Here, the semiconductor is assumed to be *n*-type, and the source voltage is set to ground. Under ideal conditions, the carrier concentration in the channel is sufficiently low such that no measurable current flows on application of a small positive voltage between the source and drain (V_{DS}) while maintaining a zero gate-to-source voltage (V_{GS}). For V_{GS} and $V_{DS} > 0$, electrons in the semiconductor accumulate near the semiconductor-insulator interface, trap states fill, and drain-to-source current (I_{DS}) flows. At a fixed value of V_{GS} and a small V_{DS} , I_{DS} increases in a linear fashion according to Ohms law (Figure 2.2). At higher values of V_{DS} , a charge depletion zone forms near the drain, effectively pinching off the accumulation layer and producing the observed saturation in $I_{DS} \equiv I_{DSAT}$ when $V_{DS} \ge V_{GS}$ - V_{ON} . Also, as seen in Figure 2.2, the magnitude of I_{DSAT} is determined by V_{GS} and the associated charge density in the accumulation layer (note: additional details on transistor operation can be found in Chapter 1).

In a high-performance transistor, I_{DSAT} is large even for small V_{GS} , while only a small leakage current flows through the gate insulator. I_{DSAT} is given by

$$I_{DSAT} = \frac{W}{2L} \mu C_G (V_{GS} - V_{ON})^2$$

where, *cf.*, Figure 2.1, W is the width of the transistor; L is the source-to-drain separation; μ is the channel device mobility; C_G is the gate-capacitance density; and V_{ON} is the turn-on voltage (represented as the value of V_{GS} where I_{DS} rises above the

gate leakage current). I_{DSAT} can be maximized by minimizing L, using a semiconductor with a large μ , or maximizing C_G.

For our purposes, we are interested in maximizing C_G , which is described by

$$C_G = \frac{\mathcal{E}_I \mathcal{E}_0}{d_I}$$

where ε_I is the relative dielectric constant of the insulator, and d_I is the thickness of the insulator. Higher values of C_G , leading to enhanced transistor performance, will thus be observed with thin insulators having high dielectric constants. But, these characteristics must be tempered by the need to maintain small leakage currents, which increase dramatically via tunneling for very thin films. Such leakage currents can represent a significant source of power loss in driving devices, which in the case of solution-processed and printed electronics is of considerable concern in the context of the dimensionally large transistors envisioned for use in macroelectronic applications.

At this point, it is useful to consider the important film features and performance metrics that will produce an optimal gate dielectric. The surface of the dielectric should be atomically smooth. A dielectric with a rough surface will lead to an irregular insulator-semiconductor interface, impeding the flow of charge through the semiconductor and reducing channel mobility. As noted above, thin films with large relative dielectric constants (> ~10) and small leakage current densities (< ~10 nA/cm² @ 1 MV/cm) are desirable. At the same time, large breakdown fields (> ~4 MV/cm) are required to preserve device function. To achieve the necessary leakage currents and breakdown fields, films must be as dense as possible and exhibit no pores or

cracks. Both from the perspective of surface smoothness and need for high breakdown fields and low leakage currents, amorphous films are generally preferred for the fabrication of gate dielectric layers.

Because of the challenges in producing such insulators via solution methods, it should not be surprising that most oxide semiconductor²⁻⁵ and solution-processed inorganic TFTs⁶⁻⁸ have been fabricated by using binary oxide gate insulators, e.g., SiO₂, Al₂O₃, Y₂O₃, or HfO₂, formed via thermal oxidation or vapor deposition; TFTs containing inorganic semiconductors in conjunction with solution-deposited thin organic/inorganic hybrid dielectrics have also been described.⁹⁻¹¹ Although binary oxides will continue to be used for TFT gate dielectric applications, they do not represent an optimal approach to realizing high-performance devices. Binary oxides have a tendency to crystallize,^{1,12} many at low process temperatures, producing grain boundaries that contribute to enhanced impurity interdiffusion and high leakage currents. An important gate insulator figure-of-merit is provided by the product of the dielectric constant and breakdown field.¹³ It is important to note that binary oxides with high dielectric constants have small band gaps, and binary oxides with small dielectric constants have wide band gaps. Wide band-gap oxides are desirable for gate dielectrics, as breakdown fields scale with the magnitude of the band gap. But, these are generally the materials with small dielectric constants. Hence, selection of a binary oxide as an insulator involves a compromise between dielectric constant and breakdown field.

One approach to the production of high-performance dielectrics relies on the use of mixed-metal, multiple- component oxides. These oxides provide convenient means for controlling the dielectric-constant breakdown-field product through incorporation of components that specifically contribute to performance via dielectric constant or breakdown. At the same time, the mixed materials can inhibit crystallization, resulting in deposition of amorphous films with extremely flat surfaces. Common candidate, base oxides for tuning these properties are listed in Table 2.1.

The oxides SiO₂, Al₂O₃, and related wide band-gap binary oxides are attractive for use at the channel-semiconductor interface, because their large gaps and attendant conduction-band discontinuities contribute to high breakdown fields and suppression of charge injection. Oxides such as HfO₂, Ta₂O₅, and TiO₂ exhibit relatively small band gaps, but they are highly polarizable, which translates into high and desirable dielectric constants. But, their modest band gaps and high electron affinities contribute to small conduction-band offsets at the insulator-semiconductor interface, providing small carrier injection barriers, low breakdown-field capabilities, and high leakage current densities.

Multiple-component oxides can be used in three ways to meet the performance requirements of gate dielectrics in TFTs. A single homogeneous dielectric can be produced by combining selected wide band-gap materials with those exhibiting smaller gaps and higher dielectric constants. For example, the mixtures $HfO_2-SiO_2^{14}$ and $HfO_2-Al_2O_3^{15}$ have been extensively studied as gate dielectrics in Si CMOS devices. Alternatively, wide and small-gap materials can be interleaved to form

multilayered structures, as demonstrated by stacked layers of TiO_2 and Al_2O_3 produced via atomic layer deposition. The presence of sharp dielectric interfaces in such structured materials provides a means to improve dielectric-breakdown fields. Finally, a compositionally graded material dominated by a high dielectric-constant material at the metal-insulator interface and a high band-gap material at the dielectric-semiconductor interface provides an additional alternative.

Producing High-Quality Films from Solution

The production of high-quality insulators is predicated on the deposition of porefree, crack-free oxide films. The fundamental challenges in depositing oxide thin films from solution are associated with the processes of conversion of soluble precursors into dense solids. This statement should be intuitively obvious, but without appropriate reaction pathways between the liquid and solid states, high-quality films cannot be produced. The prevalence of morphologically coarse oxide films in the literature reveals that suitable chemistries have not been applied to many oxide systems. The failure of many precursor systems results from addition of a variety of condensation inhibitors and surface capping groups that effectively stabilize reactant species under a variety of processing conditions. In the majority of such cases the modifications produce high energy barriers to reaction, precluding low-temperature conversion to solid oxide and promoting the production of high surface-area, porous, and rough films. By placing greater emphasis on conversion pathways from precursor to oxide, low energy reactions should be devised that allow condensation to proceed uniformly. Especially for electronic applications, thin oxide films must retain density, homogeneity, and uniformity during condensation, so identification of appropriate conversion pathways represents the primary prerequisite for success.

Typically, in solution-phase film deposition, a precursor coating is applied to a surface and heated, whereupon the elimination of solvent leads to localized crystallization and separation of solid particles. To prevent these processes, metalorganic precursors can be commonly employed for "sol-gel" deposition, wherein the organic ligands essentially act as vehicles to promote glass formation. Ultimately, embedded organic ligands must be removed from thin-film layers, either by rapid combustion or slow diffusion. Rapid combustion generates a high density of reactive surfaces, which leads to pinholes and voids that must be eliminated via high-temperature densification. Alternatively, the organic ligands at depths of greater than a few nm. Further removal of organic groups can only occur through cracks and voids in the film. So the required mass transport limits the quality of deposited films, their deposition rates, or thickness per deposition cycle.

In principle, high-quality films could be deposited at a high rate if appropriate precursors were available. We have designed a class of aqueous inorganic precursors that exhibit chemical reactivities that are especially suitable for high speed processing. Namely, the precursors described in the following sections undergo rapid condensation, and they resist crystallization without addition of organic ligands.

HafSOx Thin-Film Dielectrics¹⁶

Hafnium oxide sulfate (HafSOx) was chosen as a candidate oxide dielectric because the system exhibits diverse chemistries in solution, and it resists crystallization in the solid phase.

In addition, as noted above, oxides containing HfO₂ are well known to have relatively high dielectric constants. The strong interactions between hafnium-hydroxo groups (and analogous zirconium-hydroxo groups) and sulfato ligands have been known for a century,¹⁷ but solution species have only been characterized under special conditions or inferred from structural characterization of precipitated crystals. Through variations in concentration, temperature, and time, the nature of solution-phase condensation can be controlled to be molecular, colloidal, gelatinous, or nanocrystalline.¹⁸⁻²¹ All of these forms of hafnium oxide sulfate become amorphous as they dehydrate, and in fact, crystallized phases have not been synthesized by solid-state reaction. Therefore, the material can readily be prepared in the amorphous state and remain so over a great range of conditions, providing a convenient path to the desired morphology of a dielectric film.

A simplified series of reactions between a hafnium salt and sulfuric acid is given in Figure 2.3. The reactions showcase important facets of thin-film synthesis (but don't address the precise identities of intermediates or complexities of aqueous hafnium chemistry.) In the first step, a hafnium oxide chloride crystal hydrate is dissolved in water to disperse small hafnium-hydroxo molecular clusters. Sulfato ligands are subsequently added in the form of sulfuric acid. Since sulfato binds more strongly than chloro, hafnium-hydroxo-sulfato aqueous species are created. Under mild heating, these species readily polymerize through dehydration to form amorphous thin films. During drying, changes in pH accentuate condensation of already reactive clusters. Hence, long-range covalent bonding proceeds before localized rearrangements and "mud cracking" can occur.

The condensation chemistry allows films of various compositions, as the addition of sulfate renders the materials amorphous over a range of concentrations as implied by the acronym HafSOx, where "x" typically assumes values of 0.3-1 (refer to Figure 2.3, where the top reaction sequence represents x = 0.5.) The amorphous character and structural integrity are retained until the material decomposes with stoichiometric loss of SO₃(g) at approximately 700 °C. The smoothness and uniformity of deposited films are illustrated by the SEM images in Figure 2.4. Rapid kinetics, absence of organics, and facile condensation, all play important roles in the deposition of these dense HafSOx films.

The rapid condensation processes also allow for a variety of metal-atom substitutions within the amorphous matrix, including but not limited to Al, Ca, Ce, and La. HafSOx thin-films and several atomically mixed compositions at thicknesses of 150–250 nm were studied as dielectrics in metal-insulator-metal (MIM) capacitor structures. Such MIM structures were constructed by depositing the insulator on Ta metal, *cf.*, Figure 2.4, and adding an array of Al contacts of 1.2-mm diameter via thermal evaporation. At a frequency of 1 kHz, dielectric permittivities of 9–12, and loss tangents < 1% have been established for all variations, exhibiting little

dependence on composition. Breakdown fields of 4-6 MV cm⁻¹ have been demonstrated with leakage currents < 10 nA cm⁻² at 1 MV cm⁻¹. Selected materials have been evaluated as gate dielectrics within TFT structures, where the other component films of the TFTs have been deposited by conventional vapor methods. For this application, the dielectric must provide effective modulation of current in the adjacent semiconductor layer; any significant mobile charge in the dielectric will hamper operation. In the example provided here, La atoms were included in the matrix (HafSOx:La) in an attempt to nominally raise solution pH without premature particle agglomeration, thereby lowering levels of residual chloride and minimizing mobile charge in the dielectric. Operational characteristics of a resulting TFT are illustrated in Figure 2.5a. These results represent the first successful incorporation of a solutiondeposited oxide gate dielectric in a functioning inorganic TFT. The device behaves in a qualitatively ideal manner. Current levels are effectively modulated with applied gate voltage; and at each gate voltage, drain current increases predictably until saturation. More importantly, gate leakage currents are so low that a large on/off ratio $(\sim 10^{7})$ in the transfer curve (Figure 2.5b) can be attributed to effective switching rather than undesirable current across the dielectric. Transfer and measured gate leakage (I_G) curves, such as those given in Figure 2.5b, are only occasionally reported in the literature, yet they represent a fundamental contribution to establishing the veracity of reported TFT function. The ordinate I_D, here and in any I-V curve for a transistor, simply represents the total drain current, which arises from both the desired charge flow through the semiconductor channel and any unwanted leakage through the

dielectric. As a result, a device with a poor dielectric and a high gate leakage current can produce apparent ideal transistor behavior similar to that illustrated in Figure 2.5a. In such devices, derived parameters such as channel mobility may be erroneously derived.

The combined characteristics of HafSOx films make them effective dielectrics. Smooth interfaces and homogeneous morphology, permittivity of approximately 10, and low leakage currents collectively allow moderate voltage operation, while alleviating energy losses from gate leakage. The preparation temperature of 325 °C is relatively low, considering that organic sol-gel precursors usually require heating to \geq 500 °C and/or oxygen plasma ashing for conversion to oxides.

AIPO Thin-Film Dielectrics

The system Al₂O_{3-3x}(PO₄)_{2x} (AIPO) offers unique opportunities for realizing highperformance dielectrics, both in terms of precursor chemistries and solid phases.²² Hydrolysis of Al⁺³ solutions is known to generate molecular hydroxo clusters through condensation,^{23,24} whereas the addition of phosphate oxoanions produces heteropolymeric species, although these have been studied in much less detail.²⁵ Precursors from these reactions may be readily synthesized over a wide composition range, relying on the dissolution of aluminum hydroxide in a mineral acid, as facilitated by polymeric interactions of Al⁺³ with phosphate ligands supplied in the form of phosphoric acid. Thin liquid films deposited from these solutions undergo prompt condensation and partial dehydration with mild heating, forming a dense oxide framework as solvent molecules are eliminated. Kinetically rapid condensation and non-disruptive hydroxo diffusion facilitate a flexible, additive deposition strategy that is not accessible with kinetically hindered sol-gel processes. The nominal reaction occurring during the coating and curing of a fully dehydrated film with an electrically useful composition may be expressed as:

$$\mathrm{Al}(\mathrm{OH})\mathrm{Cl}_2(\mathrm{aq}) + \frac{1}{2}\mathrm{H}_3\mathrm{PO}_4(\mathrm{aq}) \rightarrow \mathrm{AlO}_{3/4}(\mathrm{PO}_4)_{1/2}(\mathrm{s}) + 2\mathrm{HCl}(\mathrm{g}) + \frac{1}{4}\mathrm{H}_2\mathrm{O}(\mathrm{g})$$

In cured films, as in the solid state, stoichiometric AlPO₄ is physically and structurally similar to various phases of SiO2, while covalent Al-rich oxide compositions maintain the morphology of a glass under aggressive thermal processing (>1000 °C). In the SEM images shown in Figure 2.6a, a dense amorphous AlPO film cured at 275 °C is distinguishable from the high-quality thermally grown SiO₂ substrate only by the small difference in electron density. Because a long-range, strong covalent framework results from condensation at low temperatures, the films are structurally coherent with only mild heating. Thus, although short-range relaxations are possible, long-range diffusion, segregation, and roughening do not accompany subsequent solvent loss, which is apparent from the retention of film quality following nondisruptive dehydration (Figure 2.6b). Here, the film is ramped nearly instantaneously from 275 to 600 °C without cracking or pore formation, all while undergoing a 15% volume reduction. Importantly, these glasses may also accommodate a large fraction (*ca.* 33 at%) of a less acidic oxide, such as La_2O_3 , which provides enhanced polarizability and dielectric constant, albeit at the expense of phase segregation above 800 °C.

The insulator-semiconductor interface is critical for transistor performance, as the number of charge trapping defects scales with interfacial area. The surfaces of AIPO dielectrics produced through inorganic condensation are essentially featureless, making them suitable for bottom gate TFT configurations. Rapid high-temperature processing does not alter film morphology across the entire temperature range 275–1000 °C; contact-mode AFM surface and line-profile scans of an AIPO film annealed at 1000 °C are shown in Figure 2.7. Rms roughness remains <0.1 nm, and a line-scan over 7 μ m indicates a maximum height variation <1 nm. These surfaces compare favorably with thermally grown SiO₂ dielectrics processed near 1000 °C, ²⁶ all the more impressive given the low-temperature deposition (< 275 °C) and subsequent stability with respect to rapid high-temperature processing.

Morphology and structure are relevant only so far as they influence dielectric performance, which can be definitively analyzed only through device integration. Capacitance-voltage, capacitance-frequency, and current-voltage measurements are typically performed using metal-insulator-metal (MIM) or metal-insulator-semiconductor (MIS) capacitor structures.²⁷ Such characterization, although useful for extracting basic leakage current density, permittivity, and breakdown data are not, by themselves, sufficient analysis of functionality. Furthermore, because of widely varying requirements with respect to device area, test structures must be of an appropriate size to reflect potential applications. Selected I-V curves extracted from MIM and MIS devices with spin-coated AIPO insulators are depicted in Figure 2.8. Leakage current density (J_{leak}) at a field strength of 1 MV cm⁻¹ is <10 nA cm⁻² for 185-

nm thick AIPO films processed at 300 °C with accompanying breakdown fields ≥ 6 MV cm⁻¹. The thermal flexibility of the multicomponent system is evident in that rapid annealing to 1000 °C results in *reduced* leakage with improved dehydration. While MIS devices are not ideal test structures because of the potential growth of an interfacial SiO₂ layer, current profiles of MIM capacitors with M = Ta and Al are essentially identical to those on Si for temperatures where the metals are chemically and morphologically stable (T ≤ 350 °C).

This thermal stability comes with a price, however, as low polarizability of the covalent matrix imparts a modest dielectric constant of ~5 for Al₂PO_{5.5} compositions, (though substitution of 33 at% La can boost this value to ~8.5). This suboptimal value can be somewhat mitigated by high breakdown fields and low leakage currents. As demonstrated by use in Si CMOS devices for more than 30 years, low-leakage insulators with (relatively) low permittivity, e.g., SiO₂, can offer capacitance densities suitable for high-performance applications, provided they can be deposited sufficiently thin without compromising breakdown and leakage characteristics.

There are very few methods, aside from expensive and slow atomic layer deposition (ALD), that are suitable for depositing high-quality ultra-thin films over large areas and hence the interest in solution processing as a potential path to high-performance oxide dielectrics. In fact, thin (<100 nm) insulators build on a major strength of film deposition through aqueous inorganic condensation, i.e., nanodimensional control in the *z* direction. As discussed in the following section, this methodology is eminently suited for facile nanolaminate fabrication requiring repetitive deposition of layers as

thin as ~3 nm with subnanometer precision. Obviously the device sizes (and attendant leakage) compatible with manufacturable solution patterning methods for macroelectronics may preclude extremely thin dielectrics on the scale of CMOS processing. Nevertheless, AIPO films as thin as 25 nm offer insulator characteristics superior to those of many thicker (>100 nm), high-permittivity oxide films deposited via conventional vapor methods. We have successfully characterized such films in MIS devices having capacitor areas of 1.1 mm², i.e., device areas that are easily consistent with the dimensional capabilities of ink-jet, microcontact, and other lowcost printing methods. Low-field leakage in these thin insulators can actually be lower than that observed in thicker films, cf., Figure 2.8, which appears to be aided by enhanced dehydration of ultra-thin layers at intermediate temperatures. Dielectric breakdown while diminished, remains acceptable at 3-5 MV cm⁻¹. In comparison, J_{Leak} and breakdown values (though not dielectric constant) are equivalent or superior to ALD-deposited dielectrics of similar thickness that are being considered for use in large-area oxide electronics fabricated via conventional physical vapor deposition $(PVD).^4$

Integration in active-channel TFTs is the decisive test of gate dielectric performance, as both current modulation and minimal leakage are required. By combining a single solution-processed layer with other components deposited though conventional vacuum methods a comparative analysis of substituted layers is possible. Even limited by the difficult dehydration common to alumina-based systems, AlPO gate insulators ~185 nm thick offer qualitative TFT performance in rf-sputtered ZnO-

channel TFTs for processing temperatures as low as 300 °C. For the device curve shown in Figure 2.9, an on-to-off ratio of 10^5 is achieved in concert with hard saturation in the I_D–V_{DS} curves. Importantly, leakage current at 40 V_{GS} is ~0.1nA. A small amount of counter-clockwise hysteresis is observed in the reverse V_{GS} sweep of the transfer curve, which may be attributed to residual hydration as acidic protons are repelled from the dielectric-semiconductor interface. Similar residual solvent or counterion contamination remains a major barrier to realizing metal oxide dielectrics with processing temperatures <300 °C. Gate-bias induced carrier trapping can impart a similar, opposite hysteresis, raising the possibility that this effect, while nominally undesirable, could be useful to stabilize or counteract the I–V effects of such trapping.²²

Higher processing temperatures permit more complete dehydration, especially when curing thinner films, and mute the aforementioned hysteresis. I-V characteristics of a TFT integrating a 40-nm AlPO gate dielectric cured at 600 °C and an rf-sputtered Zinc Tin Oxide³ (ZTO) channel are shown in Figure 2.10a. An identical device on 100 nm of thermally grown SiO₂ is shown in Figure 2.10b. Hysteresis for the AlPO device is small, and I_{DSAT} is > 600 μ A at comparatively low operating voltages (V_{GS} = V_{DS} = 10 V). Importantly, I_G values remain more than five orders of magnitude lower (~1 nA). As expected, current drive at equivalent V_{GS} is higher for the AlPO device, which has a capacitance density ~3x that of the SiO₂. Current increases are amplified in disordered semiconductors such as ZTO, where field-effect mobilities are strongly dependent on gate bias (accumulated charge density).^{28,29} In this particular case, when

biased at $V_{GS}-V_{on} = 10$ V, ZTO field-effect mobility on the SiO₂ dielectric is ~15 cm² V⁻¹ s⁻¹, whereas on the AlPO dielectric it is ~25 cm² V⁻¹ s⁻¹.

Potential chemical interactions across dissimilar solvent systems and the sensitivity of oxide semiconductors to redox conditions and surface adsorption combine to make integration of solution-processed dielectrics and semiconductors a non-trivial undertaking. By maintaining appropriate aqueous deposition conditions for each component, however, such difficulties can be minimized. Application of related solvation and condensation principles to multicomponent oxide semiconductors has allowed fabrication of high-performance oxide TFTs with solution-processed channel and dielectric. Field-effect behavior of a bottom-gate TFT composed of a 60-nm AlPO dielectric layer and an indium gallium zinc oxide³⁰ (IGZO) channel is illustrated in Figure 2.11, where both layers were deposited by spin coating and all processing and testing was performed in air at a maximum temperature of 450 °C. TFT operation remains exceptional, as the relatively high mobility (> 4 cm² V⁻¹ s⁻¹) and current drive (140 μ A at V_{GS} = V_{DS} = 15 V) are coupled with gate leakage < 1 nA, negligible hysteresis, and moderate operating voltages. These and related devices offer the highest reported performance for oxide TFTs with integrated solution-processed channels and dielectrics, and they clearly demonstrate the potential for solutiondeposited oxide electronics.

Although current processing temperatures for AlPO dielectrics remain above the threshold for plastic substrates, they are well within the thermal budget of a number of other substrates of interest for large-area applications. Further, by emphasizing film quality and the chemical prerequisites for multicomponent oxide film deposition, the potential for qualitatively ideal solution-deposited dielectrics has been established. Additional, new processing conditions and chemical modifications that will facilitate lower dehydration and precursor decomposition temperatures are readily envisioned.

Compositionally-Graded and Laminated Structures

As noted in previously, additional methods to control dielectric behavior include compositional grading and highly structured laminates. The laminates should contain multiple, discrete layers of different materials that are selected to maximize the product of dielectric constant and breakdown field. On the basis of high-temperature approaches and compromised morphologies of traditionally processed solutionderived films, the multilayer, laminated approach to structured dielectrics would be deemed impractical. The processing conditions and film qualities described in this contribution, however, have provided a means to deposit for the first time via solution such laminates, exhibiting qualities that are unsurpassed by any other known deposition technique. As shown by the TEM image of Figure 2.12, films of HafSOx and its zirconium analog ZircSOx can be interleaved to form very high-resolution, high-order multilayer structures. An accurate bilayer thickness within the laminate can be readily determined from X-ray reflectivity (XRR) measurements, which also provide confirmation of the abrupt interfaces (<0.2 nm by XRR) that are visually evident in Figure 2.12. While we have not fully characterized the physical properties of the laminates, they do offer unique opportunities for development of highly structured dielectrics.

For tuning purposes, individual film thickness can already be varied in a controllable manner from 3 to several hundred nm. In addition, the film stack can be deposited with variable levels of hydration, providing explicit control over film interdiffusion. For example, high-order dehydrated stacks exhibiting stability to high temperatures can be produced by dehydrating individual films during each deposition step. Alternatively, stacks can be initially deposited at low temperatures with retention of water and then subsequently heated at higher temperatures to promote intermixing, providing pathways to the formation of selected compositions or compositionally graded films; in addition, differential crystallization of individual films can be harnessed to fabricate crystalline high-dielectric films interleaved with amorphous low-leakage films. Here, the unique precursor chemistries and condensation processes are providing an entirely new, cost-effective bench-top approach to the deposition, study, and development of oxide films with capabilities currently unknown with conventional vapor-based methodologies.

Summary and Perspective

We have provided a brief overview of activities directed toward solution processing of high-quality oxide dielectrics. By addressing issues in precursor formation and condensation processes, oxide films of high morphological quality and performance have been successfully incorporated into functioning TFTs. Under appropriate conditions, performance characteristics of solution-processed films meet or exceed those achievable with the most advanced vapor-deposition technologies. We have demonstrated an approach for depositing on the bench top ALD-quality structures by using beaker chemistries, pipettes, and inexpensive deposition tools. Many opportunities await examination in the continuing development and study of these materials, both through the generation of new precursors and film compositions and the continued evolution of processing and printing conditions. The new ability to deposit high-quality laminates having controlled levels of hydration provides an unprecedented method for fabricating unique structured dielectrics. It is expected that rearrangements at interfaces of chemically distinct hydrates will create regions of unique ordering. Such self-assembly would augment the nanostructure of deposited layers or lead to complete blending as multinary phases. Of course, this film deposition and development vehicle has many implications beyond structured dielectrics.

Future, widespread use of such solution-derived oxide films will likely be dictated by continued progress in lowering process temperatures and demonstrating effective printing and patterning techniques for the fabrication of stable devices and circuits. At present, we have identified no fundamental issues restricting the application of aqueous-based inorganic inks via common patterning techniques that cover length scales from nano to macro. For all-oxide electronic devices and circuits, where the performance characteristics of the component oxide films are likely to be considerably affected by the use of conventional photolithography with polymer resists, direct additive processing via printing could provide a unique opportunity to demonstrate the power of solution processing and patterning. An all-oxide approach also eliminates vacuum processing, while producing films and devices that are stable, chemically robust, and environmentally benign. The new, demonstrated ability to readily deposit ultra-thin films in air at modest temperatures also provides a unique platform for fabrication of high-performance transistor devices, where, for example, exceptionally short source-to-drain lengths (<10 nm) could be realized through vertical integration of robust and simple materials sets.

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Figure 2.1 Schematic representation of a staggered, bottom-gate thin-film transistor.



Figure 2.2 Idealized I-V curves for a thin-film transistor (TFT) at increasing gate voltages V_{GS} .



Figure 2.3 Chemical sequence representing deposition of hafnium oxide sulfate, and generalized formulation for "HafSOx".



Figure 2.4 SEM of HafSOx thin film on Ta metal layer. Top layer deposited by spincoating and annealing at 325 °C for 10 min in air.



Figure 2.5 Device characteristics for bottom-gate TFT with HafSOx:La gate dielectric. The gate is evaporated Ta metal on a Si substrate. The gate dielectric is spin-coated HafSOx:La, deposited by spin-coating and annealing at 325 °C. Sputtered zinc indium oxide serves as the semiconductor layer, and source/drain contacts are evaporated Al.



Figure 2.6 Cross sectional SEM images of an AlPO film deposited on SiO₂ and cured at a) 275 $^{\circ}$ C, and b) flash annealed to 600 $^{\circ}$ C.



Figure 2.7 Contact-mode AFM surface and line-profile scans of a 148 nm AlPO film on Si after a 1000 °C anneal for 5 min.



Figure 2.8 Current voltage curves for selected AlPO capacitor structures. A highquality thermally oxidized SiO₂ dielectric in an identical structure is included for reference. Top contacts are 0.011 cm² Al dots thermally evaporated via shadow mask. Bottom contact is made via conductive substrate: p++ Si in the case of 600 °C AlPO and SiO₂ capacitors, and sputtered Ta metal for 300 °C AlPO devices.



Figure 2.9 Log(I_D)-V_{GS} (V_{DS} = 20 V) and (inset) I_D-V_{DS} characteristics for an rfsputtered ZnO TFT on a spin-coated AlPO dielectric annealed at 300 °C. V_{GS} is stepped from 0–40 V in 5 V increments for I_D-V_{DS} curves; device W/L = 5; L = 100 μ m.


Figure 2.10 Representative $log(I_D)-V_{GS}$ behavior of an rf-sputtered ZTO-channel TFT on a) 40 nm AlPO, and b) 100 nm SiO₂ gate dielectrics on unpatterned p++ Si gate electrodes. Channel and Al S/D contacts were defined with shadow masks. Dielectric films were annealed at 600 °C prior to channel deposition, and the completed stack annealed at 300 °C.



Figure 2.11 a) Transfer curve and gate leakage and b) output characteristics for a bottom-gate TFT with solution-processed IGZO-channel and 60-nm AlPO gate dielectric on an unpatterned p++ Si gate electrode. Maximum processing temperature for the device is 450 °C.



Figure 2.12 TEM cross-sectional image of a HafSOx/ZircSOx nanolaminate, consisting of 16 alternating layers (8 bilayers) with HafSOx on the SiO₂/Si substrate. HafSOx layers of 8.6 nm and ZircSOx layers of 5.3 nm together compose bilayers of 13.9 nm.

Oxide	Dielectric Constant	Band gap (eV)		
SiO ₂	4	8.9		
Al_2O_3	9	8.7		
HfO_2	25	5.7		
Ta_2O_5	26	4.5		
TiO ₂	80	3.0		

Table 2.1 Properties of selected binary oxide gate dielectrics.

Chapter 3

SOLUTION PROCESSED ALUMINUM OXIDE PHOSPHATE THIN-FILM DIELECTRICS

Stephen T. Meyers, Jeremy T. Anderson, David Hong, Celia M. Hung, John F. Wager, and Douglas A. Keszler

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Abstract

Aluminum oxide phosphate thin films have been deposited via spin coating from aqueous solution and utilized as gate dielectrics in thin-film transistors. Films are atomically smooth, dense, and amorphous, while exhibiting excellent morphological stability to 1000 °C. Film chemistry and structure are investigated by using an array of analytical techniques including X-ray diffraction, FT-IR spectroscopy, and electron-microprobe analysis. Dielectric film functionality and quality are explored through integration in capacitor and thin-film transistor devices. Film permittivity for an Al₂PO_{5.5} composition is found to be 4.8 in combination with leakage currents < 10 nA cm⁻² at 1 MV cm⁻¹ and current limited breakdown fields up to 10 MV cm⁻¹. Thin-film transistors fabricated with these oxide phosphate dielectrics and sputtered ZnO channels exhibit strong field-effect and current saturation with incremental mobilities up to 3.5 cm² V⁻¹s⁻¹. The ability of the amorphous matrix to accommodate additional oxide components is demonstrated by the incorporation of La₂O₃ and a resulting increase in film permittivity to 8.5, while maintaining breakdown fields > 4 MV cm⁻¹.

Introduction

Digital fabrication of thin-film electronics and micro-electromechanical systems (MEMS) via high-speed printing of solution-processed film stacks is an attractive alternative to conventional vapor deposition, especially for ultra low-cost and largearea applications. While much of the research in this field has focused on smallmolecule and polymer-based organics, theoretical studies, and all practical results to date, indicate a relatively low performance ceiling for these materials.¹⁻⁴ In contrast, inorganic materials offer potential performance several orders of magnitude higher. Indeed, promising results have been reported on the solution-phase deposition of silicon, chalcogenide, and carbon-nanotube semiconductors as transistor channels; though integration, environmental, and device-stability issues have yet to be addressed.⁵⁻⁸ Given recent advances in vacuum deposited oxide semiconductors,^{9,10} stable and complementary solution-processed all-oxide devices offer a new approach, provided suitable deposition chemistries are developed. An operational solutionprocessed oxide gate dielectric represents a vital part of this vision, and the stringent requirements on film quality and electrical characteristics make it a challenging target and key development milestone. In this contribution, we describe the solution deposition and processing of such a high performance gate dielectric.

Thin-film transistor (TFT) gate dielectrics must be smooth, dense, free from pinholes and charge trapping defects, and exhibit low leakage current under applied bias. Many of these same attributes are also desirable for a wide range of applications both within and beyond traditional thin-film electronics, e.g., memory devices, passive components, and corrosion barriers. The singular importance of a superior oxide dielectric is best illustrated by the universal adoption of Si in conventional microelectronics, not for its quite ordinary semiconductor attributes, rather for the extraordinary insulating characteristics of its native oxide.¹¹ The modest, bias-dependent mobilities of disordered semiconductors and high voltages encountered in contemporary thin-film devices render the need for low-leakage dielectrics even more acute for large-area applications. In fact, the lack of analogous low-cost oxide dielectrics suitable for macro-area additive processing is a major obstacle to the realization of ubiquitous macroelectronics.¹²

The chemical requirements for solution-phase deposition of homogenous metal oxide films were suggested more than 40 years ago.¹³ Nevertheless, the aforementioned morphological constraints imposed upon a thin-film transistor (TFT) gate dielectric have proven difficult for solution-processed oxides to overcome. Common techniques using metal-organic precursors require controlled hydrolysis in combination with stabilizing ligands and organic solvents, which are typically decomposed and expelled under heat.¹⁴ The disruptive volume loss following from these requisite high-temperature anneals often lead to discontinuities, surface roughness, and crystallization.¹⁵ Moderate TFT performance necessitates minimal leakage current across the dielectric, rendering such defects fatal to transistor functionality. Recently, surface-mediated solution processes and layered oxide nanosheets have been advanced as means to achieve the necessary film quality for high- κ Si applications.^{16,17} In addition to unproven device integration, however, the

limited growth rates, throughput, and process flexibility of these methods make them incompatible with macro-area additive processing. The approach taken in this contribution relies on fostering native $M-(OH)_x-M$ interactions within an aqueous precursor solution by controlling pH, limiting high-volume ligands and non-functional counterions, and preventing formation of large sol particles. These metastable hydroxo-frameworks allow smooth, hydrated films to rapidly dehydrate through a series of hydroxide condensation reactions, forming glassy products without pore formation or cracking. Using a similar methodology, we recently reported the first practical direct deposition of an inorganic, aqueous solution processed medium- κ oxide dielectric.¹⁸ As a corollary to these investigations, aluminum oxide phosphate (AIPO) films of the general formula $Al_2O_{3-3x}(PO_4)_{2x}$ have been fabricated and their dielectric properties evaluated.

In many ways, aluminum is an ideal candidate metal for a solution-processed oxide dielectric because of its well known propensity to form polymerized hydroxonetworks in aqueous solution and dense amorphous oxide dielectrics via vacuum methods.¹⁹⁻²² However, the direct dissolution, deposition, and hydrolytic decomposition of soluble aluminum salts generally results in poor quality oxide films. AlPO₄, though less polarizable than Al₂O₃, is interesting for its marked structural and physical similarities to SiO₂. Furthermore, the tendency towards polycation condensation and gel formation within aqueous Al⁺³–PO₄⁻³ systems has been well documented,^{23,24} providing evidence of the strong interactions possible in hetero-polycation solutions. In this context the use of aluminum-phosphate interactions to enhance aqueous solubility, morphology, and curing characteristics for aluminumbased films is relatively unexplored, despite its first suggestion by Rothon over 20 years ago.²⁵ Instead, most studies to date have used metal-organic precursors in nonaqueous pyrosol processes, delivering poor quality aluminum phosphate films unsuitable for extensive dielectric analysis.²⁶⁻²⁸ Here, we have used simple acidic cation hydration chemistry to design aqueous aluminum phosphate-based heteropolycation precursors. These solutions undergo prompt condensation with applied heat to form oxide films with morphologies and electrical performance generally possible only through expensive high vacuum methods. Initial discussion will be directed to elucidation of the composition and atomically dense morphologies observed in AIPO films, followed by their consequent dielectric properties and seminal use in qualitatively ideal TFTs.

Experimental

Synthesis. Precursor solutions were prepared by dissolving Al(OH)₃ (Alfa) in two molar equivalents of HCl (aq) (EMD, ACS 37%) or HNO₃ (aq) (Fisher, ACS 70%) (for La modifications only) and the appropriate amount of H₃PO₄ (aq) (Fisher, ACS 85%). Al(OH)₃ dissolution was accomplished by stirring under moderate heat (80–90 °C) in a water bath for 24 h. La:AlPO precursor solutions were prepared by dissolving La₂O₃ (Cerac 99.9%) in the preceding HNO₃-based solutions (up to 33% of the total metal ion concentration.) Total metal ion concentrations ranged from 0.1 to 1M; 18-MQ Millipore water was used for the preparation of all solutions.

Film Preparation and Characterization. Thin films were prepared by depositing precursor solutions on Si substrates and rotating at 3000 rpm for 30 s followed by an immediate hot-plate cure at 275 °C for 30 s. This deposition was repeated as necessary to obtain the desired thickness, and the process was completed with a furnace anneal in air at 275-1200 °C for 5-60 min. Film thickness per deposition cycle was dependent on both solution concentration and anneal temperature. Typical film thickness for one deposition cycle with a 0.5-M Al solution was ~38 nm following an anneal at 300 °C for 30 min. Unless otherwise noted, films were placed directly into a pre-heated furnace for the final anneal. Dielectric films were deposited on bare, p-type Si substrates (0.008–.016 Ω cm), for high-temperature analysis, or on 500-nm Ta metal sputter deposited on Si for anneal temperatures \leq 350 °C. La:AlPO dielectric films were tested on 100 nm of indium tin oxide (ITO) that was deposited via rf sputtering on Si substrates. Spectroscopy, diffraction, and chemical analyses were performed by using films deposited on 200-nm thermally grown SiO₂ on undoped Si substrates. All substrate surfaces were cleaned by sonication in a 5% solution of Contrad 70 for 45 min at 45 °C followed by a thorough rinsing with 18 $M\Omega$ H₂O. Substrates were then subjected to a 10- min oxygen plasma ash at 10 mTorr, 5 sccm O₂, and 0.75 W cm⁻² prior to spin coating.

Transmission Fourier transform infrared (FT-IR) spectra were measured on thin films by using a Nicolet 5PC spectrometer with a reference spectrum collected from a bare substrate. Thin-film X-ray diffraction (XRD) data were collected by using a Rigaku RAPID diffractometer with Cu Kα radiation. Electron probe microanalysis (EPMA) was performed with a Cameca SX-50 with wavelength dispersive spectrometers and gas-flow proportional detectors with P-10 gas. O, Si, P, Cl, and Al K α intensities were collected at accelerating voltages of 10, 15, and 20 kV, and averaged over 10 positions on each sample. SiO₂, MgO, Ca₁₀(PO₄)Cl₂, and Al₂O₃ were used as standards. Raw intensities were corrected by a procedure detailed by Donovan and Tingle.²⁹ Quantitative elemental analysis was determined by comparing experimental K-ratios to simulated values using StrataGEM thin-film composition analysis software. Film surface morphology was analyzed by using a Digital Intstruments Nanocope III Multimode atomic force microscope operated in contact mode with a Veeco NP-20 SiN probe and a scan frequency of 2 Hz. A low-pass filter and a first-order plane fit were applied to all samples to limit high-frequency noise and sample tilt.

Device Fabrication and Characterization. Metal insulator metal (MIM) and metal insulator semiconductor (MIS) capacitor test structures were constructed by spin coating AIPO films on conductive substrates as described above and then thermally evaporating 200-nm thick circular Al contacts via shadowmask (0.011 cm²) onto the dielectric. Relative dielectric constant and loss tangent in the frequency range 100 Hz – 1 MHz were determined by using a Hewlett-Packard 4192A impedance analyzer; measured dielectric constants varied by < 5% across the stated frequency range. Leakage current and breakdown fields were assessed with a Hewlett-Packard 4140B picoammeter and a voltage ramp of $1Vs^{-1}$.

Bottom gate thin-film transistor (TFT) test structures were fabricated by rf sputter deposition of 40-nm ZnO semiconductor channels on the dielectric films through a shadow mask, followed by evaporation of 200-nm Al source and drain contacts also through shadow masks. ZnO was sputtered from a ceramic target under a total pressure of 5 mTorr with a 25 sccm flow rate for both O_2 and Ar. Dielectric/semiconductor stacks were then subjected to a 1 h post-deposition anneal at 300 °C in air prior to Al deposition. Semiconductor channel length was 100 µm, and device width was 500 µm for all reported devices. SiO₂ control dielectrics in MIS devices and TFTs were thermally grown to 100-nm thickness on *p*-type Si wafers with 30 nm of Ta and 300 nm of Au sputtered on the back side to allow an ohmic contact to the gate. TFTs were characterized in the dark with a Hewlett-Packard 4156C semiconductor parameter analyzer.

Results and Discussion

Morphology and Composition. On the grounds that gate dielectric performance is heavily predicated on film morphology, a study was undertaken to determine the effect of phosphate content on film structure as deposited from a basic aluminum chloridephosphate solution. Films with an anhydrous composition corresponding to Al_2O_3 . $_{3x}(PO_4)_{2x}$ were cast from precursor solutions wherein the atomic ratio of phosphorus to aluminum (x) was varied from 0.25 to 1. The rapidly declining equilibrium solubility of aluminum at lower phosphoric acid concentrations prevented extension to x < 0.25. Stoichiometric AlPO₄ consists of tetrahedrally coordinated Al and P atoms, and it exists in several polymorphs that closely resemble SiO₂ in structure and physical properties. AlPO films deposited from solutions where x > -0.80 crystallized under mild heating (< 275 °C when x = 1) to form mixed tridymite and cristobalite AlPO₄ phases, *cf.*, Figure 3.1. The onset of crystallization was found to increase in temperature as x decreased and to be highly dependant on heating rate and thermal history. Films cast from phosphate deficient (x < -0.75) solutions remained amorphous to X-rays indefinitely when heated at 800 °C and for > 1 h at 1000 °C when ramped at 10 °C/min. Broad diffraction peaks consistent with cristobalite and tridymite AlPO₄, as well as α -Al₂O₃, are observed after 1 h at 1200 °C.

The extreme thermal stability of these amorphous oxide films is notable, even considering the relatively high activation energy commonly required for corundum nucleation from amorphous alumina. Given the high covalency of the Al-O-P matrix and the differing coordination environments for Al in Al₂O₃ and AlPO₄, this result is not entirely unexpected. Many analogous compositions consisting of covalent binary compounds substituted into more ionic and structurally dissimilar systems are known to resist film crystallization,³⁰⁻³² e.g., SiO₂ and Al₂O₃ in HfO₂. P₂O₅, though a highly covalent glass former, is not widely used in film preparation because of problematic PVD of the quasi-molecular oxide. Interestingly, the slow evaporation (at 100 °C) of bulk precursor solutions similar in composition (x = 0.5) generated powder residues that revealed significant cristobalite and tridymite content after heating at < 250 °C. Presumably, the rapid condensation and strong covalent bond formation occurring in

hot-plate cured thin films forestalls kinetically slower long-range diffusion and phase segregation otherwise favored during slower bulk dehydration and heating.

As in similar glasses, only limited changes in physical and optical properties have been reported in sputtered Al₂O₃–AlPO₄ films over a wide range of intermediate phosphate contents.^{33,34} For this reason, and to balance the need for a thermally stable, smooth, amorphous film with a reasonable preparation time, a P/Al ratio of 1/2 was chosen as a basis for dielectric testing; further references to AlPO films herein correspond to this stoichiometry. Additionally, solutions of this composition were found to maintain sufficient acidity to accommodate dissolution of less acidic metal oxides such as La₂O₃, while maintaining the necessary polymerization to produce glassy films. Solutions incorporating up to 33% La relative to the total metal-ion concentration were used to fabricate dense, smooth films that remain largely amorphous after 1 h at 800 °C (Figure 3.2). Continued heating of La-doped films induced segregation of small-domain monoclinic LaPO₄ after 1 h at 1000 °C.

As seen from the scanning electron microscope (SEM) images in Figure 3.3, AIPO films prepared from an aqueous solution with x = 0.5 exhibit a dense, smooth morphology over a wide temperature range. This is noteworthy, considering the significant volume loss observed on annealing at elevated temperatures, e.g., a 15% decrease in film thickness is observed 600 °C following an initial anneal at 275 °C. Contact-mode atomic force microscopy (AFM) imaging of identical film surfaces over a large area (25 μ m²) exposes no distinguishable features above the instrument noise floor, resulting in a root-mean-squared (RMS) roughness ≤ 0.2 nm, even for films

annealed as high as 1000 °C. Higher resolution scanning across 2.5 μ m² reveals a slight surface texture, which compares favorably to thermally grown SiO₂ dielectrics.³⁵ Figure 3.4 depicts typical AFM surface and 7- μ m line profile scans of a 150-nm AlPO film used for electrical analysis (5 deposition cycles on B-doped Si with a final anneal at 1000 °C for 5 min). The maximum height variation over the surface area shown is 0.84 nm, with an accompanying rms roughness of 0.08 nm.

No cracking or morphological deformation is observed through either form of microscopy, indicating that the glassy films maintain a degree of plasticity through the course of dehydration, allowing local rearrangement of bonds to relieve stresses. It has been previously noted that the strength of Al-O and P-O bonds allow a tilting or twisting of tetrahedra in the formation of bulk mesoporous glasses and zeolite type molecular sieves in the presence of bulky organic groups,³⁶⁻³⁸ as well as in negative thermal expansion behavior.³⁹ Such phenomena may also contribute to nondisruptive dehydration and densification. Inclusion of 33% La does not appreciably alter the surface roughness of films annealed up to 600 °C; RMS roughness values as measured via AFM were consistently ≤ 0.2 nm over 25 μ m².

To confirm the volume loss associated with annealing was primarily a result of dehydration and concurrent elimination of HCl, FT-IR spectra (Figure 3.5) were collected from films annealed at temperatures from 275 to 600 °C. The primary features of interest are the broad absorption band centered at 3500 cm⁻¹ (attributed to O-H stretching modes) and the low intensity absorption band at 1640 cm⁻¹ (attributed to H–O–H bending modes). Both features diminish in intensity with increasing anneal

temperature, leaving no observable absorption after heating the film at 600 °C. Although slightly distorted in profile because of a necessary background correction for the SiO₂ layer present on the substrate, the high intensity phosphate absorption band at 1120 cm^{-1} does not decrease in intensity.

AlPO₄ is reported to be compositionally stable under atmospheric pressure to > 1500 °C, eventually decomposing into volatile P_4O_{10} and Al_2O_3 .⁴⁰ Features in the region 1000–400 cm⁻¹ are consistent with a superposition of Al–O and P–O vibrational modes. Atomic percentages of Cl relative to Al from EPMA for annealed films are summarized in the inset of Figure 3.5. Recalling that the concentration of HCl was twice that of Al in the mother solution, it is clear that the largest fraction of Cl is eliminated during deposition and heating below 275 °C. Moreover, Cl loss is largely concurrent with dehydration in the temperature range 275 to 550 °C, and it is likely eliminated in the form of gaseous HCl. Films are largely free of Cl through hydrolytic decomposition (or oxidation) by 800 °C. Phosphate levels reflect those of the mother solution and remain constant (not shown) over the entire temperature range. While the lack of precision tracking of O in this case does not allow detailed dehydration information from EPMA, the nominal reaction occurring during the coating and curing of a fully dehydrated film may be expressed as:

$$Al(OH)Cl_2(aq) + \frac{1}{2}H_3PO_4(aq) \rightarrow AlO_{3/4}(PO_4)_{1/2}(s) + 2HCl(g) + \frac{1}{4}H_2O(g)$$

Electrical Characterization. Electrical testing of AIPO films was performed by using two basic device structures: thin-film capacitors and field-effect transistors. Initially, MIS and MIM capacitor test structures were evaluated to provide loss tangent

(tan δ) and relative dielectric constant (ε_r) values. AlPO film thicknesses were typically 135–185 nm for all devices; 100-nm thermally oxidized SiO₂ films were tested in identical devices for baseline analysis. A comprehensive tabulation of representative dielectric performance parameters is given in Table 1. The relative dielectric constant of ~4.8 for AlPO films was generally independent of anneal temperature once the largest fraction of polarizeable hydroxyl groups was eliminated below 450 °C. Loss-tangent values were consistently < 2% for dielectrics annealed at $300 \,^{\circ}$ C and sank to < 1% for dielectric films annealed at higher temperatures. Currentvoltage measurements on the same devices were used for breakdown analysis for the As catastrophic and irreversible current increases were seldom dielectric films. observed in the thin-film capacitors, a current limited "breakdown" is here defined as the field strength where leakage current density equals 10 μ A cm⁻². Current-voltage characteristics for AIPO films annealed over the range 300–1000 °C are illustrated in Figure 3.6. All films demonstrated reliable breakdown fields > 5 MV cm⁻¹ with an increase to $> 7 \text{ MV cm}^{-1}$ apparent above 450 °C. Leakage current density at 1 MV cm⁻¹ ¹ (J_{leak}) was consistently < 10 nA cm⁻². Considering the change in breakdown profile observed for AIPO films on Si annealed to 1000 °C, it is possible that breakdown characteristics were modified by an underlying interfacial oxide layer formed at this temperature. Dwell times for 800 and 1000 °C anneals were limited to 10 and 5 min, respectively, to minimize interfacial oxide growth. While the effect of an interfacial SiO₂ layer is not clear for devices fabricated at intermediate temperatures, identical

films cast on Ta substrates were found to perform similarly to those on Si after a 275 °C anneal.

La₂O₃ was dissolved in precursor solutions to produce a total La content equal to 33% of the total metal ion concentration, and thin films with this composition were deposited onto conductive ITO substrates. Dielectric analysis revealed poor breakdown characteristics at low temperatures (300 °C), possibly due to residual hydration. However, after a 30-min anneal at 600 °C La:AIPO on ITO exhibited a relative permittivity of 8.5 with associated breakdown fields > 4 MV cm⁻¹. The loss tangent (~1.2%) was slightly increased in comparison with standard AIPO compositions with J_{leak} increasing to ~18 nA cm⁻². Although only limited electrical characterization has so far been done on this and other modified AIPO compositions, these results indicate that the dielectric constant of glassy AIPO derivative films is tunable by a facile incorporation of other polarizable oxides. This is notable given that the dielectric-parameter control offered by the Al₂O₃–AIPO₄ composition itself is minimal. In a similar vein, the strong bonding properties of bulk Al₂O₃–P₂O₅ glasses have been reported to accommodate a variety of less acidic oxides, including La₂O₃.⁴¹

Field-effect thin-film transistors with AlPO gate dielectrics were fabricated and tested with rf sputtered ZnO active channels. TFT performance is assessed through an analysis of the turn-on voltage (V_{on}), drain current on-to-off ratio (I_{on}/I_{off}), and incremental channel mobility (μ_{inc}).⁴² These values afford useful figures of merit provided that qualitative TFT operation is achieved, including drain current (I_D) saturation with increasing drain-source voltage (V_{DS}), minimal hysteresis, and strong

current modulation under moderate gate bias. μ_{inc} values, calculated at 40 V_{GS} and 1 V_{DS}, are quantitatively equivalent to field-effect values and describe the mobility of carriers as they are incrementally added to the channel.

Representative characteristics for bottom-gate ZnO TFTs with AlPO gate dielectrics annealed at 300, 600, and 1000 °C, as well as thermally grown SiO₂ dielectrics, are shown in Figure 3.7. Strong gate modulation is apparent throughout the temperature range tested; drain current I_{on}/I_{off} ratios range from $\sim 10^5 - 10^6$ as dielectric anneal temperature is increased. The magnitude of the drain current and semiconductor channel mobility increase gradually with dielectric anneal temperature, presumably because of an improved interface. Interestingly, the gate leakage current (I_{GS}) does not appear to be significantly dependent on anneal temperature, suggesting that the overall quality of the films is not markedly changed. AIPO TFTs commonly exhibited gate leakage of 0.1-1 nA, while control SiO₂ devices were approximately one order of magnitude lower. It should be noted that the bottom gate electrode is not patterned for ease of processing, leading to a slightly elevated gate leakage for all devices. Mobility and current drive of AIPO TFTs were less than those observed for thermally grown SiO₂ dielectrics under all conditions. Comparable shifts in device mobility and V_{on} have been previously observed when comparing various PVD dielectrics in TFTs with ZnO channels.^{43,44} Clockwise hysteresis in ZnO channel TFTs has also been frequently reported on a variety of dielectrics, even ostensibly identical materials deposited by different methods. These effects are commonly attributed to a large density of electron trapping defects of various energies at the semiconductor/insulator

interface, and in Figure 3.7d a minimal amount of such hysteresis is evident in the SiO₂ device operation. In contrast, an opposite, counter-clockwise hysteresis is observed for AIPO devices annealed at low and intermediate temperatures (Figure 3.7a, b). In this case, the drain current on the reverse V_{GS} sweep is larger than that of the forward sweep, and a negative shift of ~2 V in V_{on} is observed. This effect diminishes gradually with increasing dielectric anneal temperature, and such hysteresis is negligible (even compared to SiO_2) for dielectric films heated above 800 °C, as demonstrated in Figure 3.7c. Nearly identical behavior has been reported for ZnO devices fabricated on thick Al₂O₃ dielectrics deposited by electron-beam evaporation,⁴⁴ and similar effects have also been characterized in MOSFET devices with SiO₂ gate dielectrics.⁴⁵ In the SiO₂ case these effects have been attributed to mobile charges associated with hydrogen impurities (protons) migrating via a hopping mechanism on bridging O atoms to the semiconductor/dielectric interface under the application of a positive potential to the gate. Given that the complete dehydration of AlOOH and Al₂O₃ species has been reported to require $T \ge 1200$ °C,²² it is probable that sufficient hydroxyl bridges are present within the mixed network of acidic phosphate/alumina tetrahedra to allow a similar migration of protons even after a moderately high-temperature anneal. The presence of large numbers of O bound protons in AIPO films at moderate temperatures is obvious from the FT-IR spectra presented above, and given the thickness of the films in question (< 200 nm), a substantive degree of hydration may be expected at temperatures well above that where significant IR absorption is observed. The hydrated character of the initially

smooth dielectric film is also likely to facilitate increased chemical interaction and diffusion during post-deposition anneals of the semiconductor. The ensuing interface is less abrupt and more likely to contain a large number of charge trapping defects, resulting in the observed trends in mobility and drive current.

Conclusion

The exceptional morphology and thermal stability exhibited by AlPO dielectric films described herein provides further evidence that appropriately tailored aqueous, all-inorganic precursor solutions offer a practical route to solution deposition of dense homogenous oxides. In these systems the prompt condensation of polymeric hydroxocations present within the as-deposited solution facilitates the rapid formation of a robust bond network, which in turn provides a kinetic barrier to particle segregation and inhomogeneities, allowing the nondisruptive elimination of solvent molecules. In the case of AIPO precursor solutions this framework is provided by formation of aluminum phosphate based heteropolycations. The viability of this approach has been demonstrated by the deposition of smooth, atomically dense dielectric films with relative dielectric constants of 4.8 and the fabrication of qualitatively ideal ZnO channel TFTs employing 148–185 nm AlPO gate dielectrics. These TFTs boast leakage currents < 1 nA and incremental mobilities of 3.5 cm² V⁻¹ s⁻¹ This performance, realized through simple, low-cost aqueous chemistries, is tolerant of aggressive thermal processing in excess of 1000 °C because of the high stability of the glassy AIPO network. Furthermore, use of the Al–O–P matrix as a tunable amorphous host for other oxides has been demonstrated by the incorporation of La_2O_3 into dielectric films with a consequent enhancement in dielectric constant.

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Figures



Figure 3.1 X-ray diffraction patterns of AlPO films prepared from solutions with the indicated stoichiometry annealed for 1 h following a 10 °C/min ramp. Simulated AlPO₄ cristobalite and tridymite patterns are included for reference. \blacklozenge Diffraction peak at 26.3° is attributed to α -Al₂O₃.



Figure 3.2 X-ray diffraction patterns of La:AlPO films prepared from solutions with a P/Al ratio 1/2 and 33% La. Films were annealed at the indicated temperature for 1 h following a 5 °C/min ramp.



Figure 3.3 Surface and cross sectional SEM images of an AlPO film deposited on SiO_2 and annealed at a) 275 °C, and b) 600 °C. On the left of each surface image a dust particle is used as a focal point on otherwise smooth, featureless films.



Figure 3.4 Contact-mode AFM surface and line-profile scans of an AlPO film used for dielectric testing. Film thickness is 148 nm on Si after a 1000 °C anneal for 5 min.



Figure 3.5 FT-IR spectra of a 183 nm AlPO film cured at the indicated temperature for 15 min. Cl content (inset) is expressed as atomic percentage relative to aluminum, as determined by EPMA.



Figure 3.6 Representative current-voltage characteristics for AlPO dielectric films. Thicknesses are the same as those listed in Table 1.



Figure 3.7 Representative $log(I_D)-V_{GS}$ behavior $(V_{DS} = 20 \text{ V})$ and (inset) I_D-V_{DS} characteristics for rf sputtered ZnO TFTs on spin-coated AlPO dielectrics annealed at (a) 300 °C, (b) 600 °C, (c) 1000 °C, and (d) thermal SiO₂ reference device. V_{GS} is stepped from 0–40 V in 5 V increments for I_D-V_{DS} curves; device W/L is 5, and L = 100 µm.

	Anneal (°C)	Thickness (nm)	tan δ (%)	J_{Leak} (nA/cm ²)	E _r	$\frac{\mu_{inc}}{(cm^2/Vs)}$	Von
	300	185	1.80	4.9	5.0	0.25	-10
AlPO	450	170	1.20	3.0	4.9	0.35	-6
P/Al	600	165	0.84	2.8	4.8	1.5	-5
= 0.5	800	155	0.80	2.4	4.8	3.5	-6
	1000	148	0.55	0.8	4.8	3.0	-1
AlPO 33% La	600	135	1.20	18.0	8.5	NA	
SiO ₂	NA	100	0.41	0.04	3.9	6.0	1

Table 3.1 Representative Electrical Characteristics of MIS Capacitors and TFTs with AIPO Dielectrics^{*a*}

^{*a*}Data from identical devices fabricated on thermally grown SiO₂ are included as a reference. μ_{inc} and V_{on} values were taken from TFTs with ZnO channels. J_{Leak} data were obtained at a field strength of 1 MV cm⁻¹.

Chapter 4

AQUEOUS INORGANIC INKS FOR LOW-TEMPERATURE FABRICATION OF ZNO TFTS

Stephen T. Meyers, Jeremy T. Anderson, Celia M. Hung, John Thompson, John F. Wager, and Douglas A. Keszler

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Abstract

A simple, low cost, and non-toxic aqueous ink chemistry is described for digital printing of ZnO films. Selective design through controlled precipitation, purification, and dissolution affords an aqueous $Zn(OH)_x(NH_3)_y^{(2-x)+}$ solution that is stable in storage, yet promptly decomposes at temperatures below 150 °C to form wurtzite ZnO. Dense, high-quality, polycrystalline ZnO films are deposited by ink-jet printing and spin-coating, and film structure is elucidated via X-ray diffraction and electron microscopy. Semiconductor film functionality and quality are examined through integration in bottom-gate thin-film transistors. Enhancement-mode TFTs with ink-jet printed ZnO channels annealed at 300 °C are found to exhibit strong field effect and excellent current saturation in tandem with incremental device mobilities from 4–6 cm² V⁻¹ s⁻¹. Spin-coated ZnO semiconductors processed at 150 °C are integrated with solution-deposited aluminum oxide phosphate dielectrics in functional transistors, demonstrating both high performance, i.e., mobilities up to 1.8 cm² V⁻¹ s⁻¹, and the potential for low-temperature solution processing of all-oxide electronics.

Introduction

The emergence of macroelectronics and a growing interest in lightweight conformal devices has spurred development of low-temperature, high-speed, digital techniques for printing thin-film transistors (TFTs). Realization of such devices is predicated on control over electronic defect states in printed semiconductors processed at temperatures ≤ 300 °C, *i.e.*, much lower than conventionally required even for vacuum-deposited inorganic materials. The well-defined electronic structure of organic small-molecule and polymer semiconductors has therefore proven attractive for low-temperature deposition via both vacuum and solution.¹⁻³ The localized nature of the molecular orbitals in these materials, however, precludes the formation of wide bands, thereby limiting carrier mobility and device performance.⁴ In contrast, carrier delocalization in inorganic semiconductors results in wide bands, high mobility, and potential device performance several orders of magnitude higher, provided defect states can be marginalized under low-temperature processing conditions. Two general have emerged for additive solution processing of inorganic approaches semiconductors at low temperatures. The first involves decoupling energetically demanding crystal growth from the printing process through the deposition of nano or microstructured materials. The second relies on tailoring reactive ink chemistries to directly produce dense films of semiconducting materials that sustain high carrier mobilities even in disordered nanocrystalline or amorphous phases. The former approach has been demonstrated with carbon nanotube, Si, and compound semiconductors:⁵⁻⁷ the latter method is typified by the deposition of metal

chalcogenides from hydrazine-based precursors.^{8,9} Despite these intriguing advances, the materials, chemistries, and processes employed therein raise serious integration, environmental, stability, and cost issues when applied to macroelectronics. Many of these concerns could be obviated through extension of the latter strategy to printing environmentally benign metal-oxide semiconductors, which have recently proven to provide high performance via physical vapor deposition (PVD).^{10,11} In terms of cost and ease of processing, polycrystalline ZnO is an especially attractive model system, as reflected in numerous PVD studies on ZnO TFTs fabricated with a wide variety of dielectrics and even on flexible substrates.¹²⁻¹⁴

In the present contribution, we demonstrate ink-jet printing of analogous devices by using low-temperature deposition chemistries to generate high-quality ZnO films. Such chemistries have not previously been demonstrated, despite the voluminous literature concerning solution-processed ZnO thin films. Reports of chemical bath deposition (CBD) are prevalent, though this process is incompatible with high-speed printing. Moreover, although careful attention to CBD thermodynamics permits the deposition of ZnO films at temperatures below 100 °C,¹⁵ TFTs fabricated by this method have thus far performed very poorly in the absence of high-temperature annealing.^{16,17} The deposition and sintering of nanoparticle suspensions following the model of decoupled growth and deposition, as outlined above, offers some advantage.¹⁸ Low-temperature sintering, however, typically results in porous nanoparticle agglomerates with a preponderance of interface states that not only limit carrier mobility, but also adversely affect TFT sub-threshold slopes, off currents, and switching voltages. Hybrid approaches using combinations of aligned nanoparticles, sol-gel,¹⁹ and CBD^{20,21} have overcome some of these density issues at the expense of process flexibility; ZnO TFTs processed at 270 °C, for example, have exhibited saturation mobilities up to 1.3 cm² V⁻¹ s⁻¹.²² Yet, to date, all purely chemical precursors compatible with high-speed printing require high-temperature (\geq 500 °C) processing,²³⁻²⁶ reflective of the high activation and diffusion energies attendant to metal-organic sol-gel²⁷ and oxidative/hydrolytic^{28,29} decomposition reactions.

In contrast to these kinetically limited, complex, and energy-intensive processes, we have advanced simple cation hydration chemistries in designing environmentally benign and highly reactive aqueous precursors for deposition of very high-quality oxide films.^{30,31} Here, purified ammine-hydroxo zinc solutions tap the rapid, low-energy kinetics of metal-ammine dissociation and hydroxide condensation/dehydration reactions to afford crystallization of ZnO near room temperature. As described herein, this minimalist approach to precursor synthesis provides superior film quality, while at the same time enabling high-throughput digital printing via ink-jet deposition. Building on our previous solution deposition of oxide dielectrics, we further demonstrate the potential for all-oxide printed electronics through fabrication of the first high-performance TFTs containing both solution-processed oxide dielectric and semiconductor layers. A ZnO semiconductor layer annealed at 150 °C is combined with a solution-processed aluminum oxide phosphate (AIPO) dielectric to yield a device exhibiting a mobility near 2 cm²/V s..
Experimental Methods

Precursor Synthesis and Analysis. Zn solutions were prepared by dissolving Zn(NO₃)₂·6H₂O (Alfa Aesar, 99.998%) in distilled H₂O to a total concentration of 0.5 M Zn. 10 mL of 2.5 M NaOH (Mallinckrodt, ACS) was added drop-wise to 15 mL of this solution over the course of 5 min while stirring vigorously. The resulting hydroxide slurry was centrifuged and the supernatant removed. The hydrated precipitate was then suspended in 20 mL of H_2O and agitated for 2 min, followed by centrifugation and supernatant removal. Rinse and separation steps were repeated four additional times to minimize Na^+ and NO_3^- concentrations. Following final centrifugation, the supernatant was decanted a final time and the hydrated precipitate dissolved in 50 mL of 6.6 M NH₃(aq) (Alfa Aesar, 99.99%) to form a stock precursor. The final Zn concentration in the stock precursor solution was 0.14 M. Millipore H₂O with a minimum resistivity of 18 M Ω was used for all dilutions and rinses. Na and impurity concentration data were generated with a Perkin Elmer 3000DV inductivelycoupled plasma optical emission spectrometer (ICP-OES). Reported data represent the mean of three consecutive replicate measurements using a minimum of two check standards to bracket measured concentrations. Bulk ZnO powders were produced for X-ray diffraction (XRD) measurements by placing a known volume of the precursor solution in a glass vial, evaporating the solvent, and dehydrating the resulting powder in a drying oven in air for 24 h at 50 °C. Powder XRD data were collected by using a Siemens D5000 diffractometer with Cu Ka radiation.

Film Preparation and Analysis. Thin films were deposited by spin coating the stock precursor solution filtered through a 0.45-µm PTFE syringe filter. Substrate rotation speed and time were 3000 rpm and 30 s. The film was then immediately cured on a pre-heated hot plate at selected temperatures between 150 and 500 °C for 5-10 min. Inks for thermal ink-jet (TIJ) printing were prepared by dilution of the stock solution with isopropanol (Aldrich, 99.5% ACS), aqueous ammonia, and H_2O to a final concentration of 5.3 M $NH_3(aq)$, 0.056 M Zn, and 40% (vol) isopropanol. Isopropanol is used solely to decrease solution surface tension to allow reliable jetting. Films were printed by promptly filling commercial Hewlett Packard (HP-80) printer cartridges and printing 1 x 15 mm lines directly onto pre-cleaned substrates at room temperature. Printing was followed by immediate hot-plate curing in air for 5-10 min at selected temperatures between 150 and 500 °C. Coating and curing steps were repeated as necessary to obtain the desired thickness. A final anneal at the same temperature was done either in air or in a tube furnace under 150 sccm flowing $N_2(g)$ Thin films for XRD and scanning electron microscopy (SEM) were or Ar(g). deposited on substrates of 200-nm thick thermally grown SiO₂ on Si. All substrates were cleaned by sonication in a 5% solution of Contrad 70 for 45 min at 45 °C followed by thorough rinsing with $18-M\Omega$ H₂O. Thin-film XRD data were collected by using a Rigaku RAPID diffractometer with Cu Kα radiation.

Device Fabrication and Characterization. Bottom-gate TFT test structures were fabricated by TIJ printing or spin coating ZnO semiconductor films of 15–40 nm thickness onto a 100-nm SiO₂ gate dielectric thermally grown on p-type Si substrates

with 30-nm of Ta and 300 nm of Au on the back side to allow gate probing through the substrate. Aluminum oxide phosphate (AIPO) precursor solutions were prepared as previously reported.³¹ 60-nm AIPO gate dielectric films were spin-coated on bare, p^{++} Si substrates and subjected to a post-deposition anneal at 500 °C for 1 h prior to ZnO deposition. 100 or 200-nm thick Al source and drain contacts were then thermally evaporated via shadow mask onto ZnO films to complete device stacks. All TFTs were characterized in the dark under atmospheric conditions by using Hewlett-Packard 4156C and 4155A semiconductor parameter analyzers; device mobility and operational parameters were evaluated following the methods of Hoffman.³²

Results and Discussion

Precursor Chemistry and Analysis. The fundamental chemical requirement for any solution printing process is the complete conversion of the precursor ink into a target oxide of the correct phase. All solvents and ligands must be eliminated under the desired processing conditions and within the thermal budget. Circuitous metal-organic routes typically sacrifice simplicity and reactivity for the sake of perceived improvements in rheological properties.²⁷ The primary result is that otherwise rapid and highly favorable reactions, i.e., the hydrolysis and subsequent hydroxocondensation of the metal species, instead require extreme activation and diffusion energies to complete. In contrast, the simplicity and reactivity inherent to aqueous Zn chemistry render an all-inorganic hydroxo-condensation approach extremely attractive. ZnO is amphoteric in nature and the weak acidity of the Zn²⁺ ion affords a

wide solubility range. The low activation energy required for $Zn(OH)_2$ dehydration and oxide crystallization is complementary to low-temperature deposition, as opposed to the much higher energies required for complete dehydration of hydroxides such as In(OH)₃ and Sn(OH)₄.^{33,34} Furthermore, Zn, in common with many borderline Lewis acids, readily forms coordination complexes with ammonia in an aqueous environment. Ammonia is distinguished from other nitrogen-based ligands by its extreme volatility and labile bonding which afford low-temperature, rapid, and (equally important) low volume-loss decomposition processes. Although the solubility of Zn in aqueous ammonia is relatively high, the kinetic obstacles to oxide dissolution are such that directly dissolving large-grain ZnO powders is difficult. Nevertheless, to fully exploit the excellent low temperature thermodynamics and rapid kinetics of ammine-hydroxo zinc decomposition, non-basic counterions must be excluded, prohibiting simple dissolution of Zn salts in aqueous ammonia. To circumvent this barrier, fresh Zn(OH)₂ precipitates may be prepared, purified, and directly dissolved in NH₃(aq) solutions. Such processes have been used for more than 80 years as part of bulk ZnO purification and synthesis procedures.³⁵ The predominant form of the aqueous ammine-hydroxo zinc complex that results depends on the ammonia concentration,³⁶ but it may be described by the general formula $Zn(OH)_x(NH_3)_v^{(2-x)+}$. Properly purified, these solutions are largely free of non-basic counterion contaminants, and precipitate a pure phase hydroxide upon ammonia loss, followed by dehydration and oxide crystallization at temperatures below 100 °C.

Synthetic conditions in the present study were intended to provide both a minimal impurity concentration, and a low-temperature, non-hydrolytic decomposition mechanism for the inevitable residual ions. Selection of the initial soluble $Zn(NO_3)_2$ salt is important in pursuit of the second goal, as polarization of the NO₃⁻ charge cloud by acidic cations is known to result in reasonably low decomposition temperatures for nitrate salts of acidic metal cations.³⁷ A study of zinc ammine hydroxide nitrates by Bénard and co-workers ³⁸ provides evidence that $Zn_5(OH)_8(NO_3)_2 \cdot 2NH_3$ and related compounds offer very low decomposition and ZnO crystallization temperatures, generally < 150 °C, with NH₃ loss occurring well below 100 °C. These results contrast starkly with thermal-analysis studies of zinc chloride hydroxide compounds including Zn₅(OH)₈Cl₂·H₂O and β-ZnOHCl by Srivastava and Secco,³⁹ which confirm the expectation that basic halides not only dehydrate at much higher temperatures than the pure hydroxides, but that hydrolytic or oxidative removal of the residual metal chloride may require significant heating, antithetical to the intended rapid, lowtemperature reaction. Precipitation conditions were likewise modified by the slow addition of a large mole ratio of a strong base (NaOH) to promote hydroxide displacement of the nitrate anion and increase precipitate purity relative to initially favored precipitation with $NH_3(aq)$. Extensive rinsing of the precipitate is employed to remove deleterious Na⁺ contaminants. ICP-OES analysis of a standard zincammine solution prepared from this precipitate after five centrifugation and rinse cycles reveals Na contamination below the 4 ppm detection limit. Dehydration of ammine-hydroxo zinc solutions prepared from these precipitates in a drying oven at 50

°C for 24 h generates a powder with the diffraction pattern seen in Figure 4.1, characteristic of large-domain hexagonal ZnO. TGA measurements on identical powders show a total mass loss <1.5 % when heated from 50–600 °C at 10° C/min, indicating substantial chemical purity following low temperature decomposition.

It is important to note that these slow bulk evaporation, dehydration, and crystallization processes are only partially analogous to the rapid, kinetically constrained printing and dehydration of hydroxide thin films. Indeed, the initial loss of ammonia under heating probably yields supersaturated $Zn(OH)_x^{(2-x)+}$ species and nucleation thermodynamics closely related to those described during CBD. However, total evaporation of the solution drives unique reactions and offers macroscopic verification of the key ink decomposition requirements for additive printing processes. A simplified precipitation, dissolution, and deposition scheme may be expressed as:

 $Zn(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Zn(OH)_2(s) + 2NaNO_3(aq)$

 $Zn(OH)_2(s) + xNH_3(aq) \rightarrow Zn(OH)_2(NH_3)_x(aq) \rightarrow ZnO(s) + xNH_3(g) + H_2O(g)$

Film Morphology and Composition. High-performance printed-semiconductor channels necessitate not only chemical and phase purity following low temperature deposition, but also a dense, homogenous morphology. While often overlooked, the influence of grain morphology and film density on the operational parameters of TFTs is difficult to overstate. This is apparent in ZnO devices fabricated from sintered nanoparticle arrays wherein individual nanocrystals may have high mobilities,^{40,41} yet carrier modulation and mobility in the TFT channel is dominated by discrete interfaces between nominally sintered nanoparticles with high surface areas and consequent

surface-stabilized shallow donors.¹⁸ Therefore, in seeking low-temperature device performance the as-deposited morphology must be as dense as possible, given that large-scale sintering and grain growth are not energetically favorable at low temperatures. SEM images of printed and spin coated ZnO films prepared from aqueous zinc-ammine precursors are seen in Figure 4.2. Printed films are considerably thinner than spin-coated films due to concentration limitations for reliable jetting and the substantial solubility of small-grain ZnO films in ammonia, which prevents successive layer-on-layer coating without an inter-layer cure of at least 300 °C. However, even thin (~15 nm) films annealed at 150 °C appear dense and continuous. Annealing to 300 °C between printing passes produces a more regular morphology, and thicker films (20 nm) with three printing passes. Repeated spincoating cycles of higher Zn concentrations, coupled with annealing temperatures of 600 °C result in ~200 nm films with large columnar grains. The dense, homogenous morphology possible from this chemistry directly correlates with high performance devices and contrasts starkly with the porous nanocrystal arrays commonly encountered in literature reports. While similar solutions have been employed in lowtemperature selective ionic layer absorption and reaction (SILAR) depositions.⁴² thermodynamics in these relatively slow surface-mediated reactions favor nucleation of isolated crystallites and anisotropic growth in selective orientations with discrete interfaces and corresponding morphologies. In contrast, the rapid kinetics of dehydration, condensation, and ammine decomposition reactions in these printed and

spin-coated films prevent long-range anisotropic particle growth, preserving film continuity.

All ZnO films in this study exhibit diffraction patterns consistent with the hexagonal wurtzite structure. Printed and spin-coated films cured at temperatures below 300 °C were extremely thin (<20 nm), preventing extensive XRD analysis beyond simple phase identification with grazing incidence diffraction. Interlayer curing \geq 300 °C allowed sequential coatings and thicker films. X-ray diffraction patterns obtained from sequentially spin-coated ZnO films annealed at 300 and 600 °C are documented in Figure 4.1. As manifest in the prominent (002) reflection observed at 34.4°, these films demonstrate a varying degree of c-axis orientation, increasing significantly with additional deposition cycles and elevated interlayer curing temperature. Substantial c-axis orientation is frequently reported following high temperature deposition of ZnO films from both solution and vapor techniques, as grain growth tends to favor the low energy (002) surface.⁴³ Although not examined in the present study, the effect of this texturing on electron mobility has been reported to be significant.²⁶

Electrical Characterization. Electrical analyses of ZnO films were performed by using the bottom-gate TFT structure depicted in Figure 4.3a. Device performance is assessed through an analysis of the turn-on voltage (V_{on}), drain current on-to-off ratio (I_{on}/I_{off}), and incremental channel mobility (μ_{inc}).³² It is imperative that all three of these parameters are optimized for a truly useful device; poor turn-on (extremely negative or positive V_{on}) characteristics are unsuitable for most circuit applications. A low I_{on}/I_{off} ratio prevents the device from operating as a high dynamic range switch,

the primary application for which TFTs are typically employed. Channel mobility directly relates to TFT current drive and maximum switching frequency, and represents a useful figure of merit provided the former parameters are acceptable. A final parameter, the subthreshold slope (S)—defined as the gate voltage required to change the drain current by one order of magnitude in the subthreshold region of the transfer curve—provides a measure of how effective applied gate voltage is in turning the channel on and off.⁴⁴

A tabulation of solution-deposited ZnO-channel TFT performance parameters representative of more than 250 devices may be found in Table 1. TFTs fabricated with spin-coated ZnO channels annealed at 300 °C in air on thermally grown SiO₂ dielectrics display promising operation, as evident from the transfer curves plotted in Figure 4.4. Strong current switching is observed for all such devices, with V_{on} values in the range -2 to 4 V, and consistent field-effect mobilities >3 cm² V⁻¹ s⁻¹ (at 40 V_{GS}). I_{on}/I_{off} ratios are ~10⁶, minimal hysteresis is observed, and for the device parameters summarized in Fig. 4.4 S = 1.3 V dec⁻¹.

Spin-coating is a valuable tool for large-area film deposition, but does not offer digital patterning and additive processing capabilities essential for high-speed printing applications. Ink-jet printing was therefore used to deposit ZnO channels for integration into TFTs on thermally grown SiO₂. Because of the physical constraints of the available commercial cartridges, isopropanol was added to stock zinc-ammine precursors to decrease solution surface tension and enable reliable jetting. As an undesirable though necessary addition from a chemical standpoint, a high volatility

alcohol was chosen to minimize the effect on hydroxide condensation reactions following deposition. No effort was made to test the resolution limits of TIJ printing for individual TFTs, rather printed channels were simple 1 mm x 15 mm stripes intended solely to demonstrate process feasibility.

TFTs fabricated from ink-jet printed ZnO channels annealed in air at 300 °C exhibited inconsistent performance with generally higher V_{on} values, increased hysteresis, and lower mobilities (~ 2 cm² V⁻¹ s⁻¹) when compared with spin-coated counterparts. This performance degradation is thought to stem from the requisite use of isopropanol in the printing process, which disrupts condensation and crystallization processes, leading to a higher density of trap states and correspondingly depressed performance.

Because the magnitude of the electrostatic barrier resulting from electron-trapping defects localized at grain boundaries in polycrystalline-channel TFTs scales inversely with carrier concentration^{45,46} significant improvements in both mobility and threshold voltage are possible by increasing the carrier concentration. Therefore, by annealing the channel in reducing conditions (analogous to oxygen partial pressure control during vacuum deposition¹⁶) oxygen vacancies and resultant additional carriers can be produced to improve device performance. Post-deposition annealing of ink-jet printed ZnO channels on SiO₂ for 1 h at 300 °C in flowing inert gas reproducibly generated transistors with field-effect mobilities from 4–6 cm² V⁻¹ s⁻¹ and current-voltage characteristics similar to those in Figure 4.5a. μ_{inc} for the device shown is 4.3 cm² V⁻¹ s⁻¹ at 40 V_{GS} and S = 0.75 V dec⁻¹, though approximately 1 V of clockwise hysteresis

remains evident. I_{on}/I_{off} is consistently > 10⁶, while hard current saturation at moderate V_{DS} values is apparent in the output curves shown in Figure 4.5b. These devices offer mobilities comparable to the highest reported for solution processed ZnO TFTs annealed at 500 °C, as well as considerably lower operating voltages (low subthreshold swing), and enhancement-mode operation (i.e., V_{on} is positive).

TIJ-printed ZnO transistors were found to exhibit strong field effect after anneals as low as 100 °C, although nonideal behavior (hysteresis, poor bias stability, and $V_{on} >$ 20 V) limited their efficacy. Qualitative TFT operation was achieved after annealing at 150 °C for 2 h in an ambient of flowing N₂; typical transfer and output curves are depicted in Figure 4.5b. Hard saturation of the output curves is again observed, indicative of efficient pinch-off of the channel. At 12 V, V_{on} is higher than desired for most applications, presumably arising from higher defect (electron trap) densities, which may also be reflected in the ~1.5 V of hysteresis in the transfer curve. μ_{inc} as calculated from the transconductance is 0.41 cm² V⁻¹ s⁻¹ at 40 V_{GS} for this device.

Annealing printed ZnO films in flowing N₂ at temperatures > 300 °C produced highly conductive channels, to the extent that after an anneal > 400 °C the channel cannot be turned off, even with a V_{GS} > -20 V. This is presumably due to the creation of a high density of oxygen vacancies and a concomitant conduction band electron density under nonequilibrium processing conditions. TFTs annealed from 400–500 °C in air are functional, exhibiting increasingly negative turn-on voltages, negligible hysteresis, and hard saturation. Current-voltage characteristics for TFTs annealed at 500 °C in air are comparable to those reported by Ong and co-workers²⁶ at similar temperatures with V_{on} near -7 V and $\mu_{inc} \sim 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The realization of printed, all-oxide electronics requires the integration of a complete printable oxide materials set, including insulators and semiconductors. To this end, bottom-gate TFTs were fabricated by spin-coating ZnO channels onto solution-processed aluminum oxide phosphate (AlPO) gate dielectric films on p++ Si substrates and evaporating Al source and drain electrodes. Detailed characterization and chemistries for AlPO dielectrics have been reported elsewhere.³¹ AlPO gate dielectrics were annealed at 500 °C prior to channel deposition; the completed dielectric-semiconductor stack was annealed for 4 h at 150 °C in air following ZnO channel deposition. Representative current-voltage curves for TFTs with 60-nm AlPO gate insulators with a relative dielectric constant of 4.8 are shown in Figure 4.6. These devices exhibit peak incremental mobilities of ~1.8 cm² V⁻¹ s⁻¹ at 15 V_{GS}, and, notably, gate leakage remains < 1 nA. The enhanced gate capacitance density ($\sim 2x$) of these AlPO dielectrics relative to the 100-nm thermally grown SiO_2 insulators used in the aforementioned devices has a significant impact on device performance. S is reduced to 0.36 V dec⁻¹ with negligible subthreshold hysteresis, while I_{on}/I_{off} remains > 10^{6} at a V_{GS}-V_{on} value of only 14 V. The excellent performance of these test vehicles notwithstanding, the elimination of the high-temperature anneal required to for the gate dielectric, as well as bias stability analysis (important for all low-temperature oxide TFTs) warrant further study. Nevertheless, we believe this device represents an important milestone in the development of printed oxide electronics, and is to our

knowledge the first reported TFT with both solution deposited oxide gate dielectric and channel layer.

The device physics of polycrystalline TFTs are dominated by grain boundary effects; the concentration of deep level defects at grain boundaries and the subsequent formation of depletion regions and double Schottky barriers facilitate both current modulation and a strong bias dependent mobility.^{45,47} Because the barrier height (and therefore device mobility) is contingent upon the interplay between carrier concentration and the energy and density of defect states, the effects of different device processing conditions can be difficult to interpret. It is commonly acknowledged that majority-carrier electrons in ZnO arise from oxygen nonstoichiometry, though the precise nature of the contributing defects, whether unintentional impurities, native structures, or surface vacancies is not well established.⁴⁸⁻⁵⁰ Considering the case of low-temperature deposition of polycrystalline films from aqueous solution, not only is the available thermal energy insufficient to induce the local bond rearrangement and diffusion necessary for minimizing gain boundary defects, but oxygen rich hydroxide intermediates in the present inks naturally result in a film with a low intrinsic carrier concentration following lowtemperature curing. The high performance of the devices in the present work may be attributed to the use of kinetically rapid and thermodynamically favorable lowtemperature decomposition to a dense oxide film, which provides a relatively small, though clearly non-trivial defect density. Increasing carrier concentrations above the low intrinsic values through intentional doping (flowing N2 anneal), or accumulating

extra carriers in the channel with higher capacitance gate dielectrics has the demonstrated potential to boost device mobility and functionality.

Conclusion

Exceptional ZnO thin films have been printed from simple and stable precursor inks based on ammine-hydroxo zinc species and integrated into active channel transistors with very limited thermal processing. Incremental device mobilities > 5 cm² V⁻¹ s⁻¹ have been achieved with moderate, 300 °C post-processing, in combination with hard current saturation, enhancement-mode operation, and on-to-off current ratios of 10⁶. These represent the highest solution-deposited oxide semiconductor device mobilities reported for any device processed \leq 300 °C. Extending the low-temperature precursor chemistry to 150 °C and integration with high-capacitance solution-processed oxide gate dielectrics has allowed printed-channel devices with mobilities of 1.8 cm² V⁻¹ s⁻¹ in tandem with hard current saturation and operating voltages < 15 V. These results, coupled with recent demonstration of solution-processed, medium-k Hf based dielectrics³⁰ demonstrate tremendous potential for the continued development of printed oxide electronics.

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Figures



Figure 4.1 X-ray diffraction pattern of a wurtzite ZnO powder obtained through decomposition of a zinc-ammine precursor ink at 50 °C in air for 24 h. This randomly oriented powder is contrasted with the increasing degree of (002) orientation observed in diffraction patterns of spin-coated ZnO films deposited via ten coating and curing cycles and annealed at the indicated temperature for 1 h.



Figure 4.2 SEM cross section and 45° tilt images of ink-jet printed ZnO thin films annealed at a) 150° C and b) 300° C. c) A spin-coated film annealed to 600° C in air.



Figure 4,3 a) Schematic structure of the bottom-gate TFT test structure used for both printed and spin-coated ZnO devices. For the device shown in Figure 4.6 the SiO_2 insulator is replaced by a 60-nm spin-coated AlPO dielectric. b) Optical microscope image of a printed ZnO-channel TFT on SiO_2 .



Figure 4.4 Log(I_D)– V_{GS} transfer and μ_{inc} – V_{GS} characteristics for a TFT with a spincoated ZnO-channel annealed at 300 °C in air. The gate dielectric for this device is 100 nm thermal SiO₂.



Figure 4.5 Log(I_D)– V_{GS} transfer and μ_{inc} – V_{GS} characteristics and I_D – V_{DS} output curves for ink-jet printed ZnO-channel TFTs on 100-nm thermal SiO₂ gate dielectrics.; channel annealed in flowing N₂(g) at (a) and (b) 300 °C and (c) and (d) 150 °C.



Figure 4.6 Log(I_D)–V_{GS} transfer characteristics (a) and I_D–V_{GS} output characteristics (b) for a TFT incorporating a 60-nm spin-coated AlPO gate dielectric ($\epsilon_r = 4.8$) annealed at 500 °C and a spin-coated ZnO-channel annealed at 150 °C in air.

Anneal (°C)	Ambient	Von	µ _{inc} (cm²/Vs)	Ion/Ioff
150	Flowing N ₂	12	0.4	10^{6}
200	Flowing N ₂	10	0.7	10^{6}
300	Flowing N ₂	3	4.3	$>10^{6}$
400	air	-1	3.3	$>10^{6}$
500	air	-7	6.1	>10 ⁶
150^{a}	air	1	1.8	10^{6}
300^{b}	air	3	3.1	10^{6}

Table 4.1 Representative Performance Parameters for Solution-Processed ZnO-Channel TFTs

^{*a*}Spin-coated ZnO on AlPO dielectric ^{*b*}Spin-coated ZnO on SiO₂ dielectric

Chapter 5

HETEROMETALLIC GROUP 13 NANOCLUSTERS AS INKS FOR OXIDE TFTS

Jason T. Gatlin, Zachary L. Mensinger, Stephen T. Meyers, Lev N. Zakharov, Douglas A. Keszler, and Darren W. Johnson.

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Abstract

A facile synthesis of discrete inorganic heterometallic hydroxo/aquo inorganic tridecameric group 13 nanoclusters is described. Organic nitroso-compounds act as reducing agents and play a key role in the formation of both $[Ga_{13}(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}](NO_3)_{15}$, and new heterometallic Ga and In Keggin-like tridaecameric $[Ga_7In_6(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}](NO_3)_{15}$ from gallium and indium nitrate salts. Both crystals are shown to afford excellent single-source solution precursors for the deposition of oxide thin films. The exceptional quality of these films is demonstrated by their integration as a channel layers in high-performance thin-film transistors.

Introduction

We recently reported a the high-yield syntheses of inorganic group 13 metalhydroxide nanoclusters, such as $Ga_{13}(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (flat-Ga₁₃, 1) and $Al_{13}(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (flat-Al₁₃).^{1,2} The M(μ_3-OH)₆M₆($\mu-OH$)₆ central fragment of these clusters forms a planar core of edge-sharing hydroxo-bridged octahedra, with six additional vertex sharing $M(\mu-OH)_2(H_2O)_4$ octahedra bound along the periphery of the core via two μ -OH bridges each. The outer metal octahedra alternate above and below the plane formed by the central seven metal ions. Prior synthetic preparation of group 13 metal-hydroxide compounds has proven difficult. Their syntheses often require caustic or acidic conditions, templating ligands and elevated temperature and pressure just to provide clusters in oftentimes low yields. Crystallization periods of months or even years have been reported.³⁻⁶ Nevertheless, the hydroxo-polymerization in the group 13 metals is better documented that most other groups; striking examples of aluminum^{3,4,6,7} and gallium^{2,5,8} complexes have been reported. Both all-inorganic and organic ligand-stabilized clusters are known, with a larger variety of ligand-supported clusters having been isolated through enhanced stability from lower charge density ligands.³

In this communication, we present an unique heterometallic gallium-indium cluster, Ga₇In₆(μ ₃-OH)₆(μ -OH)₁₈(H₂O)₂₄(NO₃)₁₅ (flat-Ga₇In₆, **2**, Figure 5.1). This compound can be synthesized reliably in yields up to 95% by utilizing two different nitroso reducing agents.^{1,2} **1** and **2** have been synthesized in gram scale quantities, enabling the unprecedented use of these nanoclusters as single-source solution precursors for deposition of oxide semiconductor thin films.^{9,10} These films have, in turn, been integrated with conventionally deposited layers to fabricate high-performance thin-film transistors (TFTs) with $In_{0.92}Ga_{1.08}O_3$ semiconductor channels.

In the case of inorganic and ligand-supported hydroxo compounds, neither heterometallic nor indium-containing clusters are known. Mixed-metal clusters are well known in the case of Keggin-Al₁₃ and Anderson-type oxo-hydroxo clusters however. The central tetrahedral metal of Keggin tridecamers can be substituted, forming M_1Al_{12} structures (M = Al, Ga, or Ge, with others suggested).¹¹⁻¹⁶ Numerous reports of central metal substitution in B-type Anderson clusters exist as well, affording $M(OH)_6Mo_6O_{18}^{3-}$ clusters (M = Al³⁺, Ga³⁺, Fe³⁺, *etc*).^{17,18} To the best of our knowledge however, no heterometallic Group 13 metal-hydroxide clusters with multiple substitution have been reported. Furthermore, the low-yielding, challenging syntheses often associated with these clusters have prevented attempts at exploring applications requiring large quantities of these compounds.

Results and Discussion

Figure 5.2 depicts synthetic routes to structures **1** and **2** using two different nitroso compound reducing agents. Applying our previously reported procedure² to $Ga(NO_3)_3$ and $In(NO_3)_3$ hydrates in a ratio of 1:12, allows isolation of single crystals of the heterometallic flat-Ga₇In₆ cluster in a 25% yield. However, the manual separation of crystals from the tar-like product mixture limits the amount of material that can be practically isolated to less than 50 mg. To address the difficult isolation

and limited reaction scale, we sought nitrosobenzene alternatives. The use of *N*-nitroso-di-*n*-butylamine affords **1** and **2** in superior yields: 85% and 95%, respectively.¹ The reaction with *N*-nitroso-di-*n*-butylamine produces a transparent oil (which can be reused in future syntheses) from which the crystalline product is easily isolated. XRD, electron probe microanalysis and preliminary mass-spectrometry data confirm that the bulk crystals isolated from the reaction and the single-crystal results reported herein are the same. Gram scale quantities of compounds **1** and **2** have been prepared using this new method. This bulk scale synthesis provides sufficient material to use these clusters as precursors for bulk materials and study their applications and properties.

As an example, we have already begun exploring the application of these clusters in solution deposition of electronic devices, which is driven by a rising interest in printed macroelectronics and the high carrier mobilities recently reported in disordered Group 13 and other p-block amorphous oxide semiconductors.^{9,19,20} Most solution precursors for printed oxide films involve controlled hydrolysis of metal-organic compounds and the condensation of metal-hydroxo "sols" that are then pyrolyzed to form the oxide. Such films are beset by a variety of density, defect, and phase segregation issues relating to the inhomogeneous nature of the sol, retention of significant organic components, or oxygen nonstoichiometry associated with organic burnout. From this perspective, soluble all-inorganic, heterometallic hydroxo-clusters, such as the flat- M_{13} system, provide model precursors, where processes are characterized largely by

hydrolysis and condensation, eliminating the detrimental effects of the organic moieties.

We have recently described all-inorganic hydroxocation condensation routes to dense, high-quality oxide dielectric films.^{21,22} On the basis of these results, the discrete hydroxide clusters 1 and 2 were immediately recognized as potential oxide precursors operating on similar principles, yet providing a prototypical system with a discrete, isolatable hydroxocation.

To test this proposition, the homometallic flat-Ga₁₃ clusters were first investigated as solution precursors. Prior to film deposition, a bulk XRD powder decomposition study was undertaken on the flat Ga₁₃ crystals. Illustrated in Figure 5.3a, the results indicate that long-range order in the crystalline Ga₁₃ hydrate is lost upon dehydration, leaving an amorphous solid. Changes in local Ga coordination with further water loss are suggested by the evolution of a broad peak near 36° 20 following heating to 200 °C. The material remains amorphous under continued heating to ~ 600 °C. By 650 °C reflections consistent with small-domain monoclinic β -Ga₂O₃ are evident.²³ Dissolution of **1** in H₂O forms a meta-stable solution which gels over a period of hours. Spin coating these solutions immediately following dissolution and curing at 200° C on an SiO₂ (200 nm on Si) substrate results in an amorphous thin film as seen in the diffraction pattern in Figure 5.3b. The gallium oxide film (*ca.* 120 nm thick) remains amorphous to at least 500° C. Following a 1 h anneal at 600° C a crystalline β -Ga₂O₃ phase is again observed.

Although Ga₂O₃ has been demonstrated as a TFT-channel material, the small size of Ga s-orbitals limits metal-metal overlap and electron mobility. Cluster 2 is therefore of particular interest because of the large In fraction and the excellent mobility observed in In₂O₃-based semiconductors. Identical solvation and spin coating of an aqueous solution of the heterometallic Ga₇In₆ clusters allowed deposition of In_{0.92}Ga_{1.08}O₃ (IGO) thin films. An SEM cross-section of such a film (cf. Figure 5.4 inset) annealed at 600 °C for 1 h demonstrates a reasonably dense morphology, although some granularity and inhomogeneities are noticeable on a ~10 nm scale. These features do not appear to correspond to crystalline domains, as the accompanying thin-film XRD pattern does not show any strong crystalline reflections. An amorphous morphology is consistent with reports of IGO films deposited via rfsputtering, which required temperatures of 700 °C to nucleate a ternary phase.⁹ It is postulated that the granular structure observed via SEM is the result of agglomeration or condensation of amorphous colloidal metal hydroxo species during spin coating. However, TEM or grazing incidence XRD measurements are necessary to confirm a definite amorphous structure.

Initial device characteristics of a TFT with an amorphous $In_{0.92}Ga_{1.08}O_3$ semiconductor derived from a spin-coated aqueous solution of **2** are presented in Figure 5.5; $V_{on} = -6$ V and limited hysteresis is observed. On-to-off current ratios are > 10⁶ for all devices fabricated on 100 nm thermally grown SiO₂ dielectrics. Fieldeffect mobilities for these bottom-gate TFTs are ~ 9 cm² V⁻¹ s⁻¹ after annealing to 600 °C for 1 h. The direct deposition of such high-performance semiconductors from aqueous solutions of molecular hydroxo clusters is unprecedented, and it represents an important step towards printed macroelectronics. Additional details on these devices will appear in a forthcoming contribution.

Conclusion

We have devised a synthetic strategy for making gallium clusters which utilizes a reusable reagent and proceeds relatively quickly, providing high yields of the cluster at ambient temperature. We have expanded this strategy and shown general utility by synthesizing aluminum clusters and heterometallic gallium/indium congeners. Insofar as these molecules might hold promise as single source precursors for novel materials (as demonstrated by the IGO thin films reported herein), developing an efficient synthetic method is highly important. Moreover, the use of discrete, identifiable, allinorganic hydroxocation precursors for oxide film deposition provides a measure of validation for the prompt inorganic condensation model proposed for oxide film deposition in other chapters. This work also perhaps sheds light on the mechanism of cluster growth: previous work suggests that dimeric or octameric fragments might form initially.⁶ Using this synthetic method, we have not observed any structure with varying compositions of the inner seven metal atoms, suggesting the M₇ core might also be particularly stable. The recent report of an analogous ligand-stabilized Fe₇ cluster supports this hypothesis.²⁴

Experimental

All chemicals were used as received: metal salts from Strem, *N*-nitroso-di-*n*-butylamine from TCI, and nitrosobenzene from Aldrich.

 $[Ga_7In_6(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (2). *N*-nitroso-di-*n*-butylamine (0.93g, 5.9 mmol 24 eq) was added to a solution of Ga(NO₃)₃ (0.068g, 0.267 mmol, 1 eq) and In(NO₃)₃ (0.872g, 2.97 mmol, 12 eq) in 10 mL methanol, and formed a homogenous solution. The mixture was evaporated at room temperature over 2 weeks, affording single crystals of **2** in 94% yield with respect to gallium. *N*-nitroso-di-*n*-butylamine was removed via syringe, and the remaining crystals were washed with cold EtOAc (three times) and dried in air. Using different Ga:In starting ratios produces clusters of the range Ga₇In₆-Ga₁₂In₁, the details of which will be presented in an upcoming manuscript.

Thin film deposition and TFT fabrication. Thin-film precursor inks were prepared by dissolving **1** and **2** in deionized water having a resistance near 18 M Ω immediately prior to deposition. This ink was deposited by spin coating on *p*-type Si substrates capped with 100 nm (TFTs) or 200 nm (XRD and SEM analysis) of thermally grown SiO₂ and cured at 200 °C for 1 min between coating steps. Coating and curing cycles were repeated 6-10x for thicker XRD/SEM films, and 2x for semiconductor channels. Film stacks underwent a final anneal for 1 h in air at the indicated temperature. Al source and drain electrodes were evaporated through a shadow mask to complete the TFT stack. TFTs were characterized in the dark using a Hewlett-Packard 4156C semiconductor parameter analyzer. *X-ray Diffraction:* Powder XRD measurements on **1** were made by using a Siemens D5000 diffractometer and Cu-K_a radiation. Thin-film XRD patterns were collected on a Rigaku RAPID diffractometer with Cu-K_a radiation. Single crystal experiments for structural determination of **2** were carried out on a Bruker Smart Apex diffractometer at 153 K using MoK_a radiation. C₆H₉₆Ga₇In₆N₁₅O₉₉ (**2**), $M_r = 3139.94$, 0.21 x 0.18 x 0.12 mm, hexagonal, *R*3 (no. 148), a = 20.6974(14) Å, b = 20.6974(14) Å, c = 18.256(3) Å, $a = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 120^{\circ}$, V = 6773(1) Å³, Z = 3, $\rho_{calcd} = 2.310$ g cm⁻³, $\mu = 3.704$ mm⁻¹, *F*(000) = 4620, $2\theta_{max} = 54.00^{\circ}$, T = 153(2) K, 16375 reflections measured, 3290 reflections independent [R_{int} = 0.0187], *R*1 = 0.0246, *wR*2 = 0.0721 for 3290 reflections (165 parameters) with $I > 2\sigma(I)$, and R1 = 0.0256, *wR*2 = 0.0727, and GOF = 1.102 for all 3290 data, max/min residual electron density +1.034/-0.406 e Å⁻³.

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Figures



Figure 5.1 Representations of the structures of $Ga_{13}(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (1) and $Ga_7In_6(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (2) as determined via single crystal XRD. Ga and In are shown as purple and green spheres, respectively; hydroxo an aquo ligands are shown in wireframe.



Figure 5.2 Reaction conditions for forming Ga₁₃ and heterometallic Ga₇In₆ clusters.


Figure 5.3 X-ray diffraction patterns for a) flat-Ga₁₃ bulk powders and b) Ga₂O₃ thin films spin coated from Ga₁₃ inks. All samples are heated in air for 1 h at the indicated temperature. Simulated β - Ga₂O₃ patterns are included for reference.



Figure 5.4 X-ray diffraction pattern of a spin coated $In_{0.92}Ga_{1.08}O_3$ film deposited via an aqueous solution of flat-Ga₇In₆ hydroxocations. (Inset) SEM cross-section of the same film.



Figure 5.5 Representative transfer and (inset) output characteristics for a bottom-gate IGO-channel TFT with a 100 nm thermally grown SiO₂ dielectric. V_{GS} in the output curve is stepped from 0–40 V in 10 V steps.

Chapter 6

AQUEOUS SOLUTION PROCESSED INDIUM GALLIUM ZINC OXIDE THIN-FILM TRANSISTORS

Stephen T. Meyers, Jeremy T. Anderson, David Hong, John F. Wager, and Douglas A. Keszler.

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Abstract

An aqueous precursor chemistry is developed to enable solution deposition of highquality indium gallium zinc oxide (IGZO) films for use as TFT semiconductor channels. In and Ga nitrate hydrates solvated in methanol are reduced by Zn and the reactive metal hydroxide nitrate condensation products are transferred to an aqueous environment for spin-coating. Solution-deposited amorphous oxide semiconductor (AOS) thin films in the In_{2x}Ga_{2-2x}O₃(ZnO)_k system with x = 0.58 and k = 0.95 are analyzed via X-ray diffraction and electron microscopy. Film functionality is explored through integration in bottom-gate TFTs with conventional SiO₂ gate insulators as well as spin coated aluminum oxide phosphate (AlPO) dielectrics. The effect of annealing temperature and time on TFT performance are examined. Enhancement-mode TFTs with spin-coated IGZO channels annealed in air at 450 °C are found to exhibit field-effect mobilities as high as 10 cm² V⁻¹ s⁻¹ at 40 V_{GS} in tandem with on-to-off current ratios > 10^6 . In the first demonstration of a TFT comprised of both a solution-processed AOS and solution processed amorphous gate dielectric exceptional performance is realized; field-effect mobilities near 3 cm² V⁻¹ s⁻¹ at 30 V_{GS}, on-to-off current ratios > 10^6 , and gate leakage currents < 25 pA are observed for IGZO/AlPO TFTs on glass substrates.

Introduction

The proliferation of flat panel displays (FPDs) across the consumer electronic space in recent years has been enabled by a rapid drop in manufacturing costs. A significant portion of these savings have been realized through economies of scale familiar to the CMOS community, including the use of ever-larger glass substrates. Future cost reductions will eventually require new high-performance materials amenable to lowcost additive manufacturing techniques to consolidate superfluous deposition, photolithography, and etch processes. Furthermore, evolution of appropriate materials and process may enable new classes of emissive, conformal, transparent, and/or flexible FPDs and other macroelectronics.^{1,2} Disordered metal oxide semiconductors have demonstrated a definite performance advantage over incumbent α -Si and competing organic semiconductor technology when processed near room temperature using conventional physical vapor deposition (PVD) methods;^{3,4} a coincident cost advantage requires the development of solution chemistries for additive printing of these oxides.

In a recent paper we described the use of simple ammine-hydroxo zinc solutions to print polycrystalline ZnO channels at low temperatures for high-performance TFTs.⁵ Likewise, most published accounts (even those with $T_{proc} > 300$ °C) of solution-processed oxide semiconductors involve simple binary nanocrystalline oxides, primarily ZnO. The reasons for this focus are many and varied. Some (low temperature crystallization/dehydration, facile nanocrystal growth, amphotericity and wide solubility range) reflect attractive attributes of ZnO itself, while others reflect the

limitations of common solution processing techniques, especially the need to avoid phase segregation of disparate cations during thermal processing. The attractive aspects of ZnO solution and solid-state chemistry notwithstanding, compelling electrical evidence from PVD film studies has emerged suggesting the grain structure of polycrystalline oxides does not offer optimal carrier mobility, process control, or environmental and bias stability,⁶ especially when processed at low temperatures. Amorphous oxide semiconductors (AOSs) containing post-transition metal cations with ns^0 electron configurations (where $n \ge 5$) have been advanced as a highperformance alternative. In these materials, diffuse, spherical, cation s orbitals dominate the conduction band minima, ensuring high electron mobility in the amorphous phase. The absence of grain boundaries and attendant high densities of surface non-stoichiometries, trap states, adsorption sites and facile oxygen diffusion Of the several Sn⁺⁴ and In⁺³ based compositions forms a second key attribute. demonstrated via PVD in AOS TFTs, 3,4,7,8 quaternary In_{2x}Ga_{2-2x}O₃(ZnO)_k (IGZO) based materials have attracted the most attention, largely due to the excellent low temperature performance and apparently stable oxygen stoichiometry and carrier concentrations afforded by the composition.⁹

Synthesis of solution-phase precursors for these multinary systems is considerably more complex than for a simple binary oxide, a fact demonstrated by the relative paucity of solution processed AOS films. The disparate charge densities and electronegativities of the cations in question lead to inhomogeneous hydrolysis and ligand lability in the solution phase, which can easily translate into the solid phase during oxide conversion. Moreover, the high dissociation and decomposition energies of the strongly bound ligands used to stabilize the cations in solution often require processing temperatures near the bulk crystallization temperatures of even these multicomponent oxides, potentially obviating the amorphous advantage. As an example several groups have deposited compositions in the ZnSnO₃ and Zn₂In₂O₅ systems using nonaqueous sol-gel precursors¹⁰ and simple chloride salt decomposition routes.^{11,12} Viability of these high temperature (500-600 °C) methods for amorphous InGaZnO₄ is improbable given a similar crystallization temperature for the quaternary oxide.^{13,14} To our knowledge, successful solution deposition and integration of amorphous InGaZnO₄ in high performance TFTs has not yet been accomplished.

In this contribution we build upon the principles of aqueous metal hydroxo condensation demonstrated previously in the deposition of $In_{0.92}Ga_{1.08}O_3$ channel TFTs from discreet heterometallic $Ga_7In_6(\mu_3-OH)_6(\mu_2-OH)_{18}(H_2O)_{24}(NO_3)_{15}$ clusters.¹⁵ In the synthetic strategy promulgated herein, nitrate hydrates are reduced with Zn metal to force hydrolysis and condensation of metal hydroxo species in a methanolic solution. The use of Zn rather than an organic reducing agent eliminates a potential source of contamination and incorporates Zn in the final oxide. By transferring the condensed product to an aqueous environment and spin coating the resulting solutions, high-performance TFTs with amorphous IGZO channels have been fabricated at temperatures as low as 350 °C. These films have demonstrated enhancement-mode operation, in tandem with field-effect mobilities as near 10 cm² V⁻¹ s⁻¹ and on-to-off ratios > 10⁶ on thermally grown SiO₂ dielectrics. Furthermore, by incorporating a

recently demonstrated aqueous dielectric precursor chemistry, TFTs have been fabricated wherein both the gate dielectric and channel layers are solution processed. These devices, fabricated on glass substrates, offer leakage currents < 0.1 nA and field-effect mobilities > $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, clearly demonstrating tremendous potential for active matrix display and other macroelectronic applications.

Experimental

Precursor Synthesis and Analysis. Methanolic solutions of In and Ga nitrate hydrates were prepared by dissolving $In(NO_3)_3 \cdot xH_2O$ and $Ga(NO_3)_3 \cdot yH_2O$ (Alfa Aesar, 99.999%) in anhydrous methanol (Baker) to a concentration of 0.24 M and 0.17 M, respectively. Metal concentrations and estimated hydration levels (x = 5.0, y = 9.3) were calculated by calcining the as-received hydrates in air at 600 °C for 8 h, and assuming formation of a stoichiometric oxide from a strict trinitrate hydrate. Zn powder (Alfa, 99.9%) was added to the solutions to bring the total metal ion concentration to 0.6 M. Reaction vials were immediately sealed following Zn addition and stirred for 48 h at room temperature. Initial Zn oxidation and dissolution was rapid and evolved a small amount of colorless gas; complete reaction took > 24 h with little or no obvious gas evolution after the first few minutes. Aliquots of the resulting clear methanolic solutions were placed under flowing Ar for 24-36 h at room temperature to evaporate the methanol. Solvent evaporation left a clear, colorless, semi-solid gel residue which appeared stable in storage under Ar for > 2 weeks at 4°C.

Thermogravimetric analyses were performed on methanolic gel residues by using a TA Instruments TGA 2950 and a 10 °C min⁻¹ ramp rate in air. Samples were pre-dried in air at 50 °C for 14 h.. Bulk IGZO powders were produced for X-ray diffraction (XRD) studies by extended drying under Ar for an additional 24-48 h, producing a foam-like powder. Powders were then calcined in a pre-heated furnace at 100-600 °C for 1 h. Powder XRD data were collected by using a Rigaku Miniflex diffractometer with Cu K α radiation. Metastable aqueous precursor solutions suitable for immediate spin-coating were prepared by dissolving gel residues in 18 M Ω deionized H₂O to a total metal ion concentration of 0.4 M.

Film Preparation and Analysis. Thin films were deposited by filtering aqueous precursor solutions through a 0.45- μ m PTFE syringe filter onto a hydrophilic substrate and rotating at 3000 rpm for 30 s. Following spin coating, films were immediately cured on a pre-heated hot plate at 300 °C for 5 min in air. Coating and curing steps were repeated as necessary to obtain the desired thickness. Final annealing was performed in a furnace under ambient atmosphere at 350–450 °C for 1-4 h with a 10 °C min⁻¹ ramp rate. Typical film thickness for one deposition cycle with a 0.4 M solution was ~15 nm following a 1 h anneal at 450 °C. Thin films for XRD and optical analyses were deposited on 1/16 in thick fused SiO₂ substrates (GM Associates). Films used for scanning electron microscopy (SEM) and electron probe micro analysis (EPMA) were deposited on Si substrates topped with 200 nm of thermally grown SiO₂. All substrates were cleaned via sonication in a 5% solution of Contrad 70 for 45 min at 45 °C followed by thorough rinsing with 18-MΩ H₂O.

Thin-film XRD data were collected by using a Rigaku RAPID diffractometer with Cu K_{α} radiation. Thin-film compositions were verified via EPMA using a Cameca SX-100 microprobe. In and Zn L_{α}, and Ga, O, Si, and N K_{α} intensities were collected at accelerating voltages of 8, 12, and 16 kV (12 and 16 kV for Ga) and averaged over 10 positions on each sample. InP, GaP, Zn, MgO, Si, and AlN were used as standards. Raw intensities were corrected for background¹⁶ and interference¹⁷ effects. Quantitative elemental analysis was effected by comparing experimental K-ratios to simulated values using StrataGEM thin-film composition analysis software. Optical spectra were obtained by using a double-monochromator grating spectrometer with Xe arc lamp source and a Si detector.

Device Fabrication and Characterization. Bottom-gate TFT test structures were fabricated by spin coating 30-nm IGZO films onto a 100-nm SiO₂ gate dielectric thermally grown on *p*-type Si substrates with 30 nm of Ta and 300 nm of Au on the back side to allow gate probing through the substrate. Conventional photolithographic techniques were used to define all IGZO channels. Bottom-gate TFTs integrating both solution processed semiconductors and dielectrics were fabricated on Corning 1737 glass using 140-nm MoW (65% Mo, 35% W wt.) gate electrodes rf-sputtered at 150 W in a 10 mtorr Ar ambient and patterned via shadow mask. Aluminum oxide phosphate (AIPO) precursor solutions (0.5 M AI) were prepared from NO₃⁻ based solutions as previously reported.¹⁸ AIPO gate dielectric films ~160 nm thick were spin-coated over MoW electrodes and subjected to a post-deposition anneal at 500 °C (100 °C min⁻¹ ramp) for 30 min prior to IGZO deposition. 200-nm Al source and drain contacts thermally evaporated via shadow mask onto the IGZO films completed all TFT stacks. TFTs were characterized in the dark under atmospheric conditions by using a Hewlett-Packard 4156C semiconductor parameter analyzer; device mobility and operational parameters were evaluated following the methods of Hoffman.¹⁹

Results and Discussion

Precursor Chemistry and Analysis. Aqueous molecular heterometallic hydroxo clusters are in many ways an ideal approach to multinary oxide synthesis. The high reactivity of these species combined with an extant hydroxo bond network limits phase segregation while providing rapid, small volume loss, and potentially low temperature condensation pathways to the oxide. Unfortunately, controlled synthesis of heterometallic hydroxo clusters has been demonstrated for relatively few cations, and then generally only under solvent and ligand conditions unfavorable for oxide film conversion.^{20,21,22} The aforementioned synthesis of $Ga_7In_6(\mu_3-OH)_6(\mu_2 OH_{18}(H_2O)_{24}^{+15}$ clusters in a methanolic solution, while a major advance in that strongly coordinating template ligands were not required, still makes use of organic reducing agents to form a discrete crystalline product. Relieved of the need to isolate and characterize a discrete crystalline product, and in the interest of incorporating Zn into the precursor, the synthetic strategy laid out in Figure 6.1 was developed. In the simplest conception heterometallic hydroxo cations normally inaccessible or unstable in water are condensed in methanol and then transferred to an aqueous environment for solution deposition. While relatively simple from a practical perspective, the combination of multiple cations solvated in a mixed protic solvent and the vagaries of nitrate reduction provide a chemical complexity which warrants a brief discussion.

Methanol is maintained as the primary solvent in Steps 1 and 2, yet the system is necessarily mixed, as H₂O from the metal nitrate hydrates supplies the hydroxo ligands required for condensation. The methanolic environment is very important in stabilizing condensed hydroxo cations which would precipitate zero-charge hydroxides in an aqueous environment. Indeed, if the nitrate reduction carried out in 2 takes place in a pure aqueous system, a gelatinous precipitate rapidly forms. The behavior of cations in mixed solvent systems is poorly understood, both due to lack of study and the extreme complexity of such solutions. However, given an estimated H_2O /cation ratio of ~5:1 for the solutions in this study relative to a ratio of > 90:1 for a simple aqueous solution, the solvent-effected limit on cation hydrolysis and condensation may be explained as a combination of related factors: a) A simple limit on the number of aqua ligands available for hydrolysis and condensation. Although the acidities of MeOH and H_2O are reduced in mixed solvent system with > 90 mol % MeOH relative to an aqueous environment, the pK_a of MeOH remains slightly lower, suggesting that at least some methoxide ions may be formed during proton reduction.²³ However, given the relatively hard Lewis acid character of the solvated cation, OH⁻ remains the favored ligand and hydrolysis product, especially when the steric limitations on methoxide condensation are considered. Thus, while potentially formed during proton reduction, methoxide ions probably play only a minor role in cluster stabilization, and are protonated on transfer of the precursor to an aqueous

environment. b) The pK_a of solvated cations tends to decrease with increasing methanol content. The enhanced electrophilic character of the cation and the nucleophilic character of bound hydroxyl groups tends to increase the degree of polymerization at a given hydrolysis reatio.²⁴ c) Changes in the polarity or charge screening properties of the solvent may allow stabilization of low charge density species. Other, kinetic solvent effects are possible, though these are assumed to be secondary given the long stirring times.

The oxidation of Zn powder in 2 provides the driving force for the synthesis. A fairly active metal, Zn is capable of reducing many species initially present in the methanolic solution, including NO_3^- , H⁺, dissolved oxygen, and even Ga^{+3} and In^{+3} species (Although Ga⁺³ and In⁺³ reduction is possible as a mechanism for electron transfer, the persistence of the metals or In⁺¹ as final products are unlikely given the oxidative potential of a 1.2 M NO_3^- solution.) To a first approximation, the precise nature of the oxidant is unimportant, as all probable oxidation reactions consume at least 2 protons per Zn atom, driving hydrolysis and condensation. In a sealed vial the concentration of dissolved oxygen is assumed to be finite and relatively small compared to the concentration of Zn (~ 0.2 M), leaving NO₃⁻ as the primary thermodynamically favored oxidizer. Nevertheless the oft-stubborn kinetics of NO_3^{-1} reduction lead to slow reactions in dilute acid, and limit interconversion of the many possible redox products with similar potentials. Coupled with the initial evolution of small amounts of a colorless gas for 5-10 minutes these kinetic barriers suggest at least initial Zn oxidation via H⁺. As the potential for proton reduction falls with increasing

pH thermodynamics favor Zn oxidation via NO_3^- as evidenced by the evolution of brown NO_2 gas when the dried gels or foams are exposed to air. To date we have not characterized the precise nitrate reduction products. Importantly, NO_3^- is also a nonchelating ligand under most conditions, leaving metal hydroxo species free to condense without template effects during initial hydrolysis reactions and in subsequent thermal curing steps.

A final, critical aspect of both solution chemistry and TFT performance is the metal cation stoichiometry applied to the synthetic scheme in Figure 6.1. Figure 6.2 combines solution chemistry and TFT performance considerations in the form of a pseudo-ternary compositional diagram outlining proposed compositional limits for precursor synthesis in methanol. In this case the vertices represent not the component oxides as in a solid state synthesis, but rather the contributing nitrate-hydrate and metal components in the methanol solution and cation stoichiometry in the oxide film. In this manner the various factors affecting precursor condensation in methanol may be combined in a single figure. It should be noted that only the composition points shown have been actively tested in TFTs or solutions to date, larger regions are proposed based on observed and expected solution and TFT behavior. Furthermore, where possible the differing H_2O /metal content provided by the various hydrates and metals has been normalized to ~5.

Several PVD investigations have been conducted on the effect of cation stoichiometry on the electrical properties of films in the $In_{2x}Ga_{2-2x}O_3(ZnO)_k$ system.^{3,25} These studies suggest that a relatively broad compositional area centered on InGaZnO₄

offers suitable electrical properties for TFT channels and an amorphous structure after processing ≤ 300 °C. This stoichiometry forms the starting point for our investigations, while the surrounding compositional space represents accessible and potentially useful cation stoichiometry (Region I). Conversely, Region II of Figure 6.2 represents a somewhat arbitrary delineation of Ga rich compositions wherein a decrease in electron mobility and carrier concentration has been documented due to limited Ga 4s participation in the conduction band and decreased carrier density.

Although much of Ga-rich Region II is accessible in the methanol solution, most of the effective cation composition space is constrained by the hydrolytic behavior of the constituent cations. For the cations in question the ionic radii increase from 67 pm for Ga⁺³ to 88 pm for Zn⁺² and 92 pm for In⁺³—a disparity of charge density matched by diverse solution and condensation chemistry.²⁶ Among the three cations, Ga⁺³ is the only one for which discrete polynuclear hydroxo cations beyond a dimer have been identified. Moreover, even in heteropolymeric Ga₇In₆ hydroxo cations the decreased charge density of hydrolyzed In⁺³ prevents formation of the 2µ₂-OH and µ₃-OH hydroxo bridges necessary for the edge linking of three octahedra in the central core.²⁷ Instead, larger In octahedra form µ₂-OH corner-sharing bridges on the periphery of the cluster. Likewise, in the present system Zn oxidation and hydrolysis of methanolic solutions in Ga-poor Region III (triangles) precipitate InOH₃/InOOH in the absence of sufficient Ga(NO₃)₃·xH₂O at identical hydrolysis ratios and a normalized H₂O content. This is perhaps the clearest direct evidence for the formation of polynuclear species: even in the MeOH dominated environment significantly hydrolyzed In^{+3} is not soluble in the absence of Ga^{+3} although the former has a nominally higher pK_a.

In comparison, we have no direct evidence for the incorporation of Zn into any polynuclear species. Rather, the primary condition governing Zn content is the extent of hydrolysis in the solutions. Region IV represents Zn-rich compositions (squares) where the rate of Zn oxidation and dissolution slows dramatically and insoluble metal hydroxides or oxides are formed. Given previous discussions of the condensation behaviors of In and Ga, the mol % of Zn in that can be accommodated is likely dependant to some extent on the ratio of those cations. (Conceivably, some portion of the Zn could be added in the form of a nitrate hydrate as well, although in this study the metal is the only Zn source.) A minimum, Zn-poor concentration is difficult to establish in the absence of NMR or other measurements to track cation condensation. Certainly, there is a minimum amount of Zn required to attain a hydrolysis ratio (OH /M⁺) great enough to force condensation of an In-Ga species. This level is imprecisely estimated defined by region V.

A final constraint on the cation and hydrolysis ratios encompassed within Region 1 is the solubility of the condensation product in H_2O following MeOH evaporation under flowing gas. This was found to be highly dependent on solvent evaporation conditions (Ar flow rate, temperature, surface area to volume ratio, etc.) as harsh conditions contributed to dehydration of hydroxo species to insoluble oxides. Precise control over experimental parameters is necessary to explore this constraint fully. Several cation stoichiometries near InGaZnO₄ were found to form clear, homogeneous

aqueous solutions with properties suitable for spin coating under a range of evaporation conditions near room temperature. IGZO-channel TFTs produced from these solutions performed similarly within the minor variations of shadow-mask defined features. An In-rich composition with a cation mol fraction of *ca*. 40 % In, 28 % Ga, and 32 % Zn (x = 0.58 and k = 0.95) was selected for further study based on consistent performance. All further results relate to this composition unless otherwise indicated.

The mechanisms by which the discrete high-nuclearity metal hydroxo clusters reported previously are stabilized with respect to the changes in coordination and hydrogen bonding undergone during solvent evaporation and crystallization are not clear; certainly the restricted conditions of their isolation indicates that stability outside the solvent environment of their formation is quite low. Isolation of crystalline species is not a prerequisite for an oxide film solution precursor; nevertheless a bulk study was made of the condensation product obtained via methanol evaporation. Extended (48-96 h) drying of a methanolic gel-precursor under Ar at room temperature yields an amorphous foam-like powder which converts to a crystalline product upon heating at 100°C for 1 h in air. The powder XRD pattern obtained from this probable nitrate hydrate (Figure 6.3) is not consistent with any combination of known nitrate hydrates or oxohydroxides, though higher-order reflections are quite weak. Structural characterization of this crystalline product has thus-far proven difficult due to limited stability and an inability to isolate a single crystal specimen. Further studies are underway, and may shed light on the structure of this hydrate and the condensed forms present in the methanol solution. Continued heating causes decomposition of the hydrate and formation of a weakly-diffracting powder with an XRD pattern consistent with small-domain trigonal InGaZnO₄ near $300 \, {}^{\circ}\text{C.}^{28}$ This oxide powder demonstrates little propensity for grain growth when heated for 1 h at temperatures < 600 ${}^{\circ}\text{C.}$

When H₂O is added to the clear gel precursor from **3**, the gel slowly dissolves to produce a clear homogeneous aqueous solution (**4**). These solutions are metastable with respect to further hydrolysis and condensation, forming translucent gels when aged for > 3 h. TGA was performed in air on both a dried aqueous gel and methanolic condensation product. The resultant mass-loss curves (*cf.* Figure 6.4) are nearly identical for both solvents, suggesting continuity of the basic composition from methanol to water. Moreover, the hydroxide nitrate is largely decomposed to the oxide < 300 °C, in contrast to previously demonstrated metal chloride AOS precursors.¹² Polarization of the NO₃⁻ charge cloud by acidic cations is provides a reasonably low temperature (and low volume-loss) decomposition pathway for residual nitrate groups,²⁹ though admittedly matrix-modified in the case of an oxide or hydroxide nitrate film. The initial mass loss from 50–150 °C is attributed to elimination of residual solvent molecules while the large mass loss from 200–300 °C

Film Morphology and Composition. Slow solvent evaporation and dehydration in bulk samples allow thermodynamic products not possible via the rapid, kinetically constrained spin-coating and thermal curing steps of film deposition. In the case of an

aqueous precursor from **3**, spin coating and annealing at 300 °C for 1 h yields an amorphous film as shown by the X-ray diffraction pattern in Figure 6.5. These 150-nm films on fused silica remain amorphous with extended heating (4 h) at 450 °C and nucleate the quaternary phase near 500 °C, consistent with the reported crystallization of rf-sputtered InGaZnO₄ films.¹³ An SEM cross section of a 120-nm film annealed at 450 °C for 4 h on thermally grown SiO₂ is shown in Figure 6.6a. The observed morphology appears dense, and is consistent from 300-500 °C. Small inhomogeneities 10-20 nm in diameter are observed in all films, and may be related to agglomeration of sub-colloidal condensation products during spin-coating, raising the possibility of further improvements to TFT electrical properties and film morphology through adjustments to precursor hydrolysis ratios. Electron microprobe analysis of thin films prepared for TFT studies confirms a cation composition within 1% of the values calculated from the solution precursors.

Electrical Characterization. Electrical analyses of IGZO films were performed by fabricating the bottom-gate TFT structure depicted in Figure 6.6b. Device performance is assessed through an analysis of the drain current on-to-off ratio (I_{on}/I_{off}) , turn-on voltage (V_{on}) , incremental channel mobility (μ_{inc}) and sub-threshold swing (S). In the primary operational mode of a transistor as a high-dynamic-range switch it is imperative that all three of these parameters are optimized. I_{on}/I_{off} , perhaps the most important parameter, should generally be > 10⁶ for both current and voltage driven applications. V_{on} —used here in place of the more ambiguous threshold voltage—is defined as the gate voltage at which an exponential increase in drain

current is first observed. For most applications a V_{on} near 0 V is preferred. μ_{inc} is a field-effect mobility calculated from the drain conductance at V_{DS} = 1 V, and quantifies the mobility of carriers in the channel as a function of applied gate voltage.¹⁹ Mobility directly relates to TFT current drive and maximum switching frequency, and represents a useful figure of merit provided the former parameters are acceptable. S is defined as the gate voltage required to increase the drain current by one order of magnitude in the sub-threshold region of the transfer curve and provides a measure of how effective applied gate voltage is in turning the channel on and off.³⁰ A tabulation of representative performance parameters for solution-deposited In_{1.19}Ga_{0.85}Zn_{0.96}O_{4.04}-channel TFTs may be found in Table 6.1.

IGZO channels spin-coated from the aqueous solutions from **6** were found to exhibit excellent performance when integrated in transistors. Log I_D – V_{GS} curves for IGZOchannel TFTs annealed in air for 1 h at 350, 400, and 450 °C are plotted Figure 6.7a Those processed at 450 °C demonstrate near PVD-quality performance with $V_{on} = 1$ V, $\mu_{inc} > 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and negligible hysteresis in forward and reverse sweeps of the gate bias. When the processing temperature is decreased by 50 °C an increase in device hysteresis (1 V) and sub-threshold swing is observed, while mobility drops slightly (4.9 cm² V⁻¹ s⁻¹). Qualitative TFT operation is, however, maintained. For TFTs annealed at 350 °C for 1 h the same cannot be said; although meager field-effect is noted, strong clockwise hysteresis and I_{on}/I_{off} of 10³ precludes effective switching; drive current and V_{on} are likewise marginal. Identical devices were fabricated and annealed at the same temperatures for 4 h to evaluate the effects of increased anneal time on channel performance. Transfer curves for these devices operated in saturation mode are plotted in Figure 6.7b. After annealing at 450 °C for 4 h incremental mobilities near 10 cm² V⁻¹ s⁻¹ are observed, in tandem with V_{on} and S values of 2 V and 0.41 V dec⁻¹, respectively. Similar modest performance gains are noted for an extended 400 °C anneal; hysteresis for these devices is negligible, while μ_{inc} increases to 6.7 cm² V⁻¹ s⁻¹. Devices annealed at 350 °C display the most obvious improvement. Where current switching was marginal under a 1 h anneal, I_{on}/I_{off} is improved to > 10⁶ and μ_{inc} is increased to 4.3 cm² V⁻¹ s⁻¹ after a 4 h anneal. ~2 V of clockwise hysteresis remains in the Log(I_{DS})–V_{GS} plot, suggesting persistence of a significant trap density.

In contrast, direct spin-coating of the methanolic solutions from 2 does not generate working TFTs at any temperature. Instead, channels are relatively conductive, with high hysteresis and off currents consistent with high-carrier densities and trap dominated conduction.

The sharp drop in TFT performance for aqueous-solution derived channels following a 1 h anneal between 350 and 400 °C does not correlate with any obvious shifts in film morphology tracked via XRD and SEM, nor with thermal decomposition of the solution precursor during TGA.

The thermally grown SiO_2 dielectrics in the test vehicles fabricated above provide useful initial characterization data for solution processed channel materials. However, realization of the low-cost digital-fabrication potential of solution processing requires integration of an all solution processed TFT film stack on a substrate compatible with large-area processing. For the semiconductor and insulator layers, amorphous oxide materials have attractive attributes in smooth interfaces, chemical robustness, and potential optical transparency. The integration of a recently developed solution processed amorphous oxide gate insulators with a spin-coated IGZO semiconductor on a glass substrate represents an initial performance proof of this goal. A 160-nm AlPO gate dielectric layer was spin coated over rf-sputtered MoW gate electrodes and annealed at 500 °C prior to channel deposition. Following spin-coating of the IGZO channel layer the completed dielectric-semiconductor stack was annealed for 4 h at 450 °C in air. Detailed characterization and chemistries for AlPO dielectrics have been reported elsewhere.¹⁸ Representative current–voltage curves for a TFT with this structure are shown in Figure 6.8. Performance is generally excellent, with gate leakage < 25 pA and $I_{on}I_{off}$ > 10⁶ at 30 V_{GS}. Peak incremental mobility at the same gate bias is 2.7 cm² V⁻¹ s⁻¹ while S = 0.64 V dec⁻¹. Very little hysteresis is observed in these devices, and hard saturation is achieved in the output curves shown in Figure 6.8b.

Conclusion

The advantages of an aqueous solution for oxide film deposition lie in the very reactivity of the cations with respect to hydrolysis and condensation; water not only solvates the ions, but takes part in the reactions that form the metal-oxide bond network. Unfortunately the very reactivity of cation-bound aquo ligands has been perceived as an obstacle to thin-film deposition because the activation energies for related precipitation and condensation processes are very similar. Moving away from the aquo ligand for solvation allows stable solutions, but can hamper oxide film formation as previously related solvent loss and condensation processes accompanying liquid-oxide conversion steps are isolated from one another. The mixed-solvent system described above makes use of both aquo-ligands for condensation and methanol for stabilization at a hydrolysis ratio not possible without precipitation in an aqueous environment. The transfer of the condensed products to an aqueous environment is possible because the kinetics of further cation condensation and are now slower than for dissolution of the already partially solvated species.

Further study of the chemistry allowing this synthesis is required, yet initial validation of this approach is evident from the high-performance devices that have been enabled. Aqueous solution processed oxide films in the $In_{2x}Ga_{2-2x}O_3(ZnO)$ system have been integrated in qualitatively superb TFTs with field-effect mobilities near 10 cm² V⁻¹ s⁻¹ and on-to-off current rations exceeding 10⁶. Moreover, these parameters have required relatively modest annealing temperatures of 350-450 °C. The prospect of a printed macroelectronics technology platform based on amorphous oxides has been further advanced via integration of solution processed IGZO semiconductors and AIPO dielectrics on glass substrates. TFTs combining these two crucial layers have demonstrated with field-effect mobilities of 2.7 cm² V⁻¹ s⁻¹ and on-to-off current rations exceeding 10⁶. Crucially, gate leakage for these devices is < 25 pA with a 160 nm AIPO gate dielectric.

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Figures



Figure 6.1 Synthetic scheme for the preparation of aqueous precursors and conversion to IGZO thin-films.



Figure 6.2 Projected compositional space compatible with the synthetic scheme laid out in Figure 6.1. Region I corresponds to compositions (\circ) were a clear homogenous methanolic solution is predicted. Region II encompasses Ga-rich compositions (\diamond) where homogenous methanolic solutions are possible, but TFT performance is expected to be poor. Region III, extrapolated from observed solution behavior, delineates Ga-poor stoichiometries (Δ) where Indium hydroxide precipitates are expected. Region IV (\Box) outlines Zn-rich compositions wherein a rising pH slows Zn oxidation and solubility. Further Zn addition is difficult and precipitates may be formed depending on In/Ga content. Region V is roughly identified with hypothesized Zn-poor compositions insufficiently hydrolyzed to drive cation condensation. H₂O/cation ratios are normalized where possible to ~5.



Figure 6.3 Bulk powder XRD patterns of a dried IGZO methanolic-gel precursor (2) heated at the indicated temperature for 1 h.



Figure 6.4 TGA mass-loss curves for bulk IGZO powders dried from methanolic and aqueous-gel precursors.



Figure 6.5 Thin-film XRD patterns obtained from 150 nm films annealed in air at the indicated temperature for 1 h (except where noted) following a 10 $^{\circ}$ C min⁻¹ ramp.



Figure 6.6 a) Cross-sectional SEM image of a 120-nm IGZO thin film annealed in air at 450 °C for 4 h with a 10 °C min⁻¹ ramp. b) Schematic structure of a bottom-gate TFT test vehicle used for IGZO channel characterization.



Figure 6.7 Representative saturation-mode $\log(I_D) - V_{GS}$ characteristics for IGZOchannel TFTs annealed in air at the indicated temperature for a) 1 h and b) 4 h.



Figure 6.8 Schematic structure of a bottom-gate TFT test vehicle integrating solutionprocessed IGZO semiconductor and AIPO dielectric layers on glass.



Figure 6.9 a) Transfer and b) output characteristics of a bottom-gate TFT on a glass substrate integrating a spin-coated IGZO channel annealed at 450 °C and solution-processed AlPO dielectric processed at 500 °C.

Anneal (°C)	Time (h)	V _{on} (V)	S (V/dec)	$\frac{\mu_{\rm inc}}{(\rm cm^2/Vs)}^a$	I _{on} /I _{off}
350	1	>25	N/A	N/A	10 ³
400	1	1	0.73	4.9	>10 ⁶
450	1	1	0.50	6.1	$> 10^{6}$
350	4	2	1.20	4.3	$> 10^{6}$
400	4	0.5	0.70	6.7	>10 ⁶
450	4	2	0.41	9.6	$> 10^{6}$
450^{b}	4	0	0.64	2.7	$> 10^{6}$

Table 6.1 Representative Device Parameters for Solution-Processed IGZO-ChannelTFTs

^{*a*}Extracted at 40 V_{GS} for devices on SiO₂ and 30 V_{GS} for AlPO devices ^{*b*}Spin-coated IGZO on AlPO dielectric

Chapter 7

CONCLUSIONS

Considering the stringent demands placed on the chemical and electronic structures of semiconductor and dielectric films via integration in a functional TFT structure, the successful fabrication of high-performance devices provides a measure of validation for the aqueous solution chemistries proposed herein. A new amorphous oxide dielectric in the $Al_2O_{3-3x}(PO_4)_{2x}$ (AIPO) system with a dielectric constant of ~5 has been developed and demonstrated in thin-film capacitor and TFT structures. Gate-dielectric function is manifest over a wide range of processing temperatures from 300–1000 °C. The nearly atomically smooth interfaces afforded by these films have permitted their use as high capacitance gate insulators less than 40 nm thick in low-leakage TFTs.

Aqueous solution chemistries have likewise been applied to the deposition of oxide semiconductor films. A low-temperature ink suitable for thermal inkjet printing of nanocrystalline ZnO semiconductor channels has been synthesized by systematically removing thermodynamic barriers to oxide conversion. TFTs with ZnO channels printed from aqueous ammine-hydroxo-zinc solutions and processed at 300 °C exhibit field-effect mobilities > 5 cm² V⁻¹ s⁻¹. Low-voltage ZnO-channel TFTs processed at plastic-compatible temperatures (150 °C) on thin AIPO dielectrics similarly display qualitative TFT operation and field-effect mobilities in excess of 1.8 cm² V⁻¹ s⁻¹.

Discrete heterometallic hydroxocations are introduced as prototypical aqueous precursors through the use of aqueous $[Ga_7In_6(\mu_3-OH)_6(\mu-OH)_{18} (H_2O)_{24}]^{+15}$ to deposit $In_{0.92}Ga_{1.08}O_3$ amorphous oxide semiconductor films. Although the TFT-channel performance of these films is high, $(\mu_{inc} > 9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ processing temperatures (600
°C) exceed optimal values. Exploitation of similar principles by forcing heterometallic condensation in a mixed solvent environment followed by aqueous dispersion and deposition affords $In_{2x}Ga_{2-2x}O_3(ZnO)_k$ based semiconductor films at lower processing temperatures. TFT test vehicles incorporating these channel layers present excellent sub-threshold characteristics and device mobilities 4-10 cm² V⁻¹ s⁻¹ following air annealing from 350-450 °C. In a culmination of these investigations the potential for solution processed oxide macroelectronics has been demonstrated through integration of AIPO dielectrics and IGZO semiconductors on glass substrates.

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