MOCVD ZINC OXIDE FILMS FOR WIDE BANDGAP APPLICATIONS

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ABSTRACT

ZnO is a wide bandgap (3.2 eV) semiconductor with potential application in LEDs, lasers, and transparent transistors, among other uses. These applications require uniform thickness, high quality materials (amorphous, poly- or single crystal), pinhole- and defect-free-single-and multilayer-conformal coatings. These attributes are generally best achievable by MOCVD. We have mounted a significant effort to develop automated MOCVD systems and process technologies for single and multicomponent oxides. The reactors use high speed rotation and are of a vertical orientation built to all metal UHV standards. We have demonstrated reactor scaled performance from 3" to 12" diameter depositions planes with modeling scales through 24" diameter. Metalorganics are used for zinc and dopant sources as well as dopant gases to optimize performance at low pressures. In this paper we will discuss our most recent results with epitaxial ZnO films, achievements in p-type doping, multilayer structures, and polycrystalline doped ZnO films.

Introduction

It is surprising that ZnO, which has a wide bandgap, has received such little attention compared to that given to semiconductors such as GaN or ZnSe. In fact, ZnO has advantages: (1) the exciton binding energy is much higher (60 meV vs 21 meV for GaN); making 300-K exciton lasing much more likely; (2) relatively large-area bulk ZnO can be grown, providing exact lattice and thermal matching to epitaxial layers (not to mention that bulk ZnO can be doped (at least n-type) or that single crystal Al_2O_3 could also serve as a substrate)[1]; and (3) wet chemical processing is routine with ZnO, but virtually impossible with GaN. One of the last major hurdles in implementing ZnO is routinely achieving and manipulating p-type ZnO.

Several deposition techniques have been applied to grow ZnO films: evaporation[2,3], r.f.[4,5,6,7], d.c.[8,9,10,11] magnetron sputtering, ion beam sputtering [12], spray pyrolysis[13,14,15], sol-gel process[16], pulse-laser deposition[17], chemical beam deposition[18], and metal-organic chemical vapor deposition (MOCVD)[19,20,21,22,23,24,25,26,27,28,29,30]. Highly conductive n-type and transparent ZnO films were readily obtained by doping with B, Al, Ga, In, and F. Al is the most commonly studied dopant in ZnO films in all growth techniques. Igasaki et al.[4] reported growth of ZnO:Al with a resistivity as low as 1.4×10^{-4} Ωcm from r.f. sputtering. Sato et al.[8] reported a resistivity of 6×10^{-4} Ωcm from d.c. sputtering. Using chemical beam deposition technique, the same group reported a resistivity of 3.4×10^{-4} Ωcm[31]. Tang & Cameron[32] obtained a resistivity of 7×10^{-4} Ωcm from a sol-gel process. Hu and Gordon[33] achieved a resistivity of 3.0×10^{-4} Ωcm from MOCVD process.

Structured Materials Industries, Inc. (SMI) has preformed extensive research on deposition of ZnO via MOCVD for a variety of applications, including displays, phosphors, scintillators,

lasers, substrates for GaN, and others. In this paper we review our most recent developments in ZnO deposition and characterization, with a particular emphasis on developments in p-type doping.

MOCVD vs. Other Deposition Techniques.

The primary methods for depositing high quality films are physical vapor deposition (PVD), spin/mist deposition, (CVD), and alternating layer (AL) CVD. PVD is a line of sight technology and is used very successfully when grading, complex multiplayer doped/mixed alloy structures, or crystalline films are not needed. The spin/mist approach is also useful for blanket coverages, but may suffer from voids or defects in thermal processing. CVD (and its refined form AL-CVD) offer tremendous advantages to other techniques in terms of conformality, grading, achievement of complex thin and multilayer structures, including epitaxial films, and its ability to adapt to deliver many complex and graded composition films. Our efforts focus on using RDR-MOCVD to produce zinc oxide films.

At SMI, we have developed Low Pressure (and Plasma Enhanced) Metal Organic Chemical Vapor Deposition (LP-MOCVD) systems to produce an array of oxides. The system employs a vertical high speed Rotation Disk Reactor (RDR), with radially distributed multi-gas-injectors on its top flange (for uniformity over large areas) and a separate oxygen injector directly above the sample platter (minimizing pre-reactions). The high speed rotating disk can be rotated through 1000 RPM. The high speed rotation and high gas velocity induces laminar, non-recirculating forced convection flow in the system. Samples are heated by a fixed radiative heater below the rotating susceptor. Thermophoresis drives particles from the deposition surface. The temperature, pressure, rotation, and mass-flow rates are monitored and controlled by a computer. A carrier gas is used to carry reactants, in vapor form, from bubbler, sublimator, or flash evaporation sources. Reactant sources and delivery lines can be temperature controlled. The carrier gas is further diluted and enters the reactor through the reactor top flange multi-inlet-injector manifold. The radially distributed injection manifold in the RDR is used to achieve radial composition grading in order to optimize thickness and composition across the deposited films. An oxidizer injector is also used for plasma enhanced mode operation in an upstream plasma column configuration for plasma enhanced CVD, as we have done with N_2, N_2O_2, and NH_3 in doping ZnO p-type. Other gases can also be introduced through this port for process enhancement. Further, the system geometry is ideal for alternating layer CVD (ALCVD). SMI has carried out extensive research and development in the deposition of ZnO with a variety of dopants, including Al, Ga, In, Si, Mn, Hf, Cu, Ta, N, Li, Mg, and others, with over 1000 deposition runs to date. Substrates have included silicon, quartz, various glass formulations, SiC, sapphire, $LiGaO_2$, GaAs, GaP, and single crystal silicon. Multilayer films with alternating layers of ZnO and (Zn,Mg)O have also been grown. For transparent conducting oxide applications, resistivity as low as 12 $\Omega/$ has been achieved. Homoepitaxial films with photoluminescence linewidths as narrow as those observed in bulk crystals (0.49 eV FWHM) were realized. These achievements are shown in Figure 1.
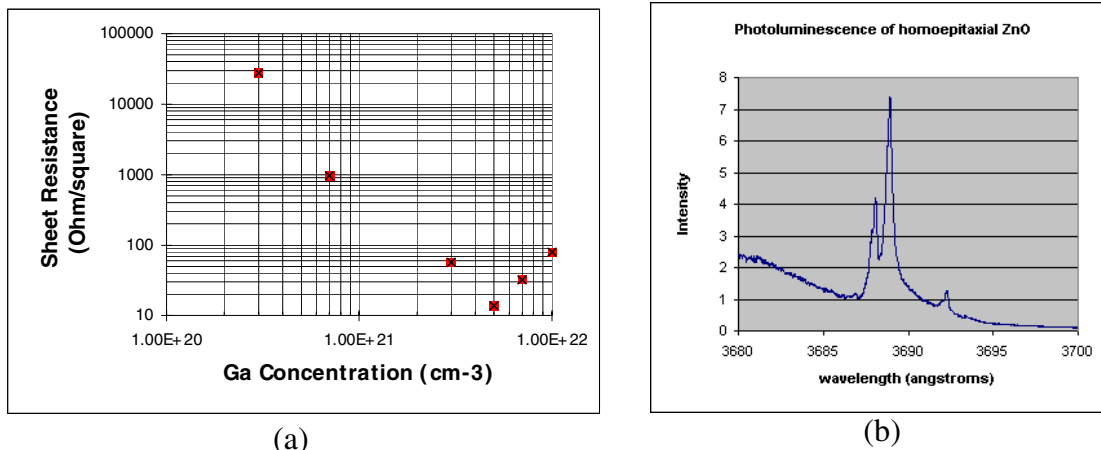
(a)

(b)

Figure 1*. Characteristics of some SMI MOCVD ZnO films: (a) resistance vs. composition for Ga-doped ZnO; (b) photoluminescence spectrum of homoepitaxial (Mg,Zn)O film; FWHM of major peak is 0.49 meV.*

p-type Doping in ZnO

The reliable availability of p-type transparent conducting oxides (TCOs) with good properties would have a wide impact in a number of fields. These materials would open the door to a new class of transparent diode devices (including detectors, and blue/UV LEDs and lasers), transistors (potentially for displays) and as alternative p-type TCOs (potentially enhancing OLEDs, photovoltaics, EL materials and so on).

Although some new p-type TCOs have recently been demonstrated based on Cu and Ag oxides,[34,35] p-type ZnO would be particularly valuable due to its high temperature stability, ease of deposition (at least ZnO in general) and patterning, direct bandgap, and availability in single crystal form for substrates. Recently, some exciting results from Japanese groups[36], Eagle Pitcher, and the University of Missouri[37] have shown promise that p-type ZnO can be made, and SMI, prior to the current study [NSF Contract DMI 9860239, Final Report], had also achieved p-type conduction in ZnO. However, reliable deposition of strongly p-type, highly conducting material using production scalable tools as needed for p-n devices has remained an elusive goal.

From our previous experience with p-type ZnO we identified trace contaminants in the films as a key factor in achieving p-type conduction. A particular goal was to avoid contaminants that could act as n-type dopants, particularly Group III elements, as well as carbon and hydrogen. See Figure 2 for a comparison of contaminant levels for previously identified p-type vs. n-type film composition depth profiles. From this prior work; the n-type nature of the film giving the data in 2 (a) was due to inadvertent Al and H doping. In order to test this contamination hypothesis, a dedicated "high purity" test reactor was fabricated with no aluminum in the construction: heating elements were fabricated of Al-free alloys, as opposed to the alloy previously used, and the wafer carrier was ceramic. Figure 3 is a SIMS depth profile from a film produced in the new system – note the low concentration of Al. This result corroborates our prior work suspicion that the Al did not come from the precursor but from the Al in the filament.
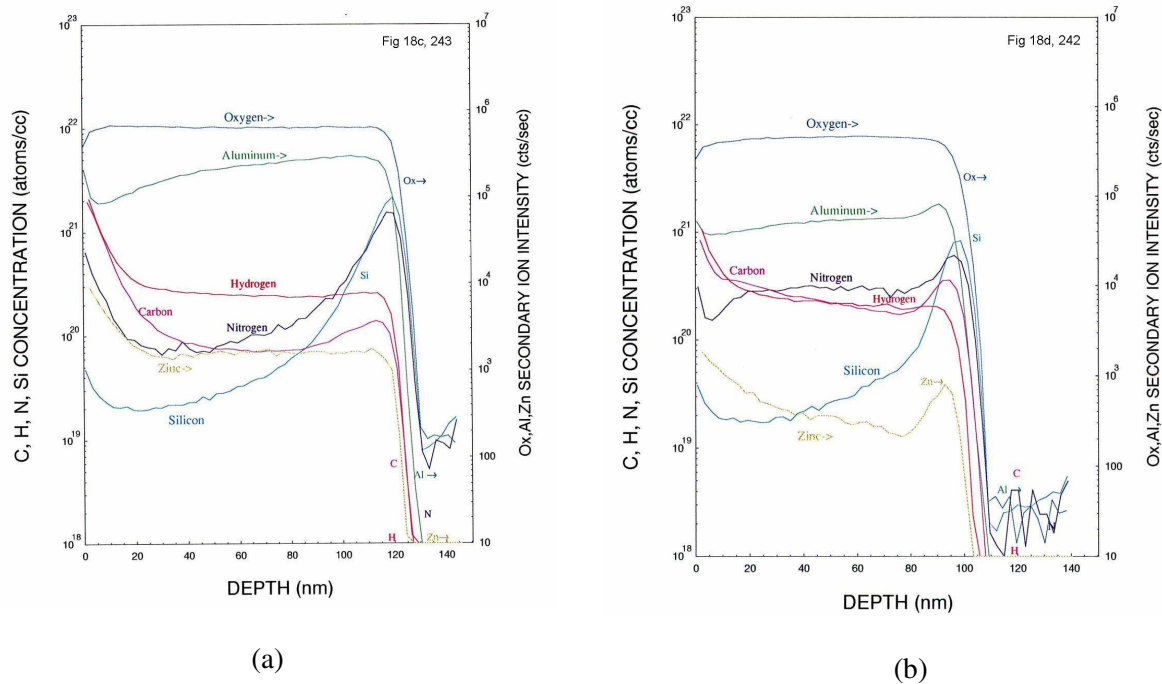
(a)   (b)

Figure 2. *SIMS depth profile for two ZnO thin films; (a) is n-type, while (b) is doped p-type with nitrogen. Note the difference in N, H, and Al levels*
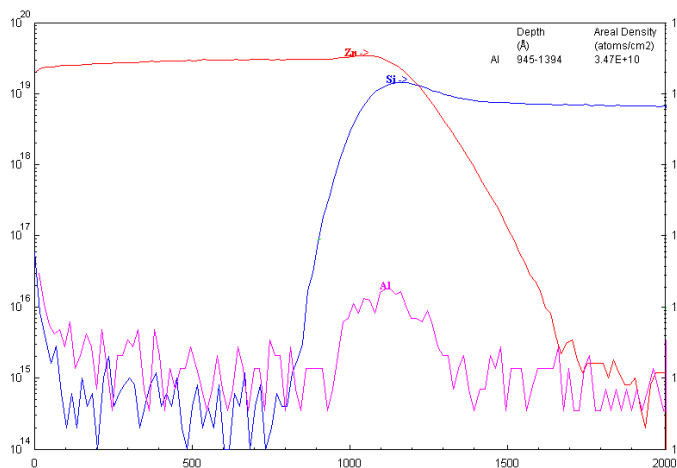

Figure 3. Zn, Al and Si SIMS depth profile for a ZnO film deposited in the new Al-free test system. Note the low Al level, barely detectable except for a very small peak at the film/substrate interface.

Films were deposited using either argon or nitrogen as the carrier gas, and oxygen was used as the oxidant. In some runs, a nitrogen plasma was used to investigate potential doping with activated nitrogen.

Process parameter ranges for the MOCVD runs performed are shown in Table 1 below.

Table 1.

Process parameter	Range
Carrier gas flow (Ar or N_2)	2500 – 4000 sccm
Oxygen gas flow	100 – 1000 sccm
Plasma gas flow / Power	0 – 200 sccm / ~70 Watts
Flash evaporator gas flow	0 – 200 sccm
Bubbler gas flow	50 – 100 sccm
Deposition temperature	350 – 550°C
Chamber pressure	10 Torr

Films were deposited on quartz substrates as undoped ZnO, and with nitrogen and lithium doping, using a metalorganic lithium source. Due to the low volatility of the lithium precursor, it was delivered using a flash evaporator as a solution in toluene.

p-type films were achieved using a variety of compositions. Films were characterized via Hall measurements performed by Dr. David Look at Wright State University. Electrical data for p-type ZnO samples produced by SMI are shown in Table 2.

Table 2. Hall data for p-type ZnO films produced by SMI via MOCVD

Sample	Composition	Type	ρ (Ω-cm)	μ (cm^2/V-s)	Conc. (cm^{-3})
a	N-doped	p	8	0.2	4×10^{18}
b	N-doped	p	54	0.6	2×10^{17}
c	(Zn,Mg)O film, background N doped	p	38	83	2×10^{15}
d	Li (~8%) and N (% unknown) doped	p	4	0.8	2×10^{19}

Summary

SMI designed and built a dedicated MOCVD reactor for the deposition of p-type ZnO, with the specific goal of eliminating aluminum contamination from the reactor components. ZnO oxide thin films were deposited under a range of processing conditions, and removal of aluminum contamination in the films from the reactor was conclusively verified. Initial deposition results are promising for optimizing routine production of p-type ZnO material.

Acknowledgements.

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