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MOCVD of Ferroelectric Thin Films

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ABSTRACT

We have examined the growth of a number of important ferroelectric oxides by MOCVD using a rotating disk reactor. Highly uniform and reproducible films over 6" wafers have been routinely achieved. Materials include Lead Zirconate Titanate (PZT, $PbZr_xTi_{1-x}O_3$), Lead Lanthanum Zirconate Titanate (PLZT), Strontium Bismuth Tantalate (SBT), $CeMnO_3$ (CMO), and others. Emphasis has been on achieving highly crystalline and oriented films at the lowest deposition temperatures possible, for compatibility with other integrated device materials and processing; and the achievement of optimum ferroelectric and pyroelectric performance. The effects of varying growth parameters, barrier and/or template layers, and post-growth annealing have been studied. The growth process, physical characterization, and ferroelectric film properties will be discussed.

Introduction

PZT thin films are capable of high pyroelectric, IR sensitivity and ferroelectric switching. The preferred device structures have limited thermal budgets. For highest sensitivity, crystalline films are required. Typically, to achieve a high degree of crystallinity this requires relatively high deposition and/or annealing temperatures. PZT deposition methods must be devised for high pyroelectric coefficient films at low temperatures, uniformly and at high rates.

In this paper we describe our recent efforts at lowering film deposition temperatures, while maintaining film quality sufficient for devices in a production scale reactor. There are several approaches to oxide film deposition; however as reviewed in Table I, specific needs must be met in order to effectively deposit such films. As shown schematically in Figure 1, MOCVD fills these needs.

Table I. Oxide Film Deposition Needs.
The deposition technology must address simple to complex oxide film deposition on flat and shaped geometries.

Method	Assessment
Sputtering	Difficult to produce epitaxy, thin films suffer from pinholes, high volume production below 0.35 μm difficult.
PLD	Deposition plane limited in scalability and deposition rates, good for rapid prototyping.
MBE	Very difficult for oxides.
Spin-on/mist	Limited with respect to complex geometries, film density and defect density.
MOCVD	Ideal for producing epitaxial, conformal, uniform, scalable, low defect, pinhole-free films, and offers ability to functionally grade the composition

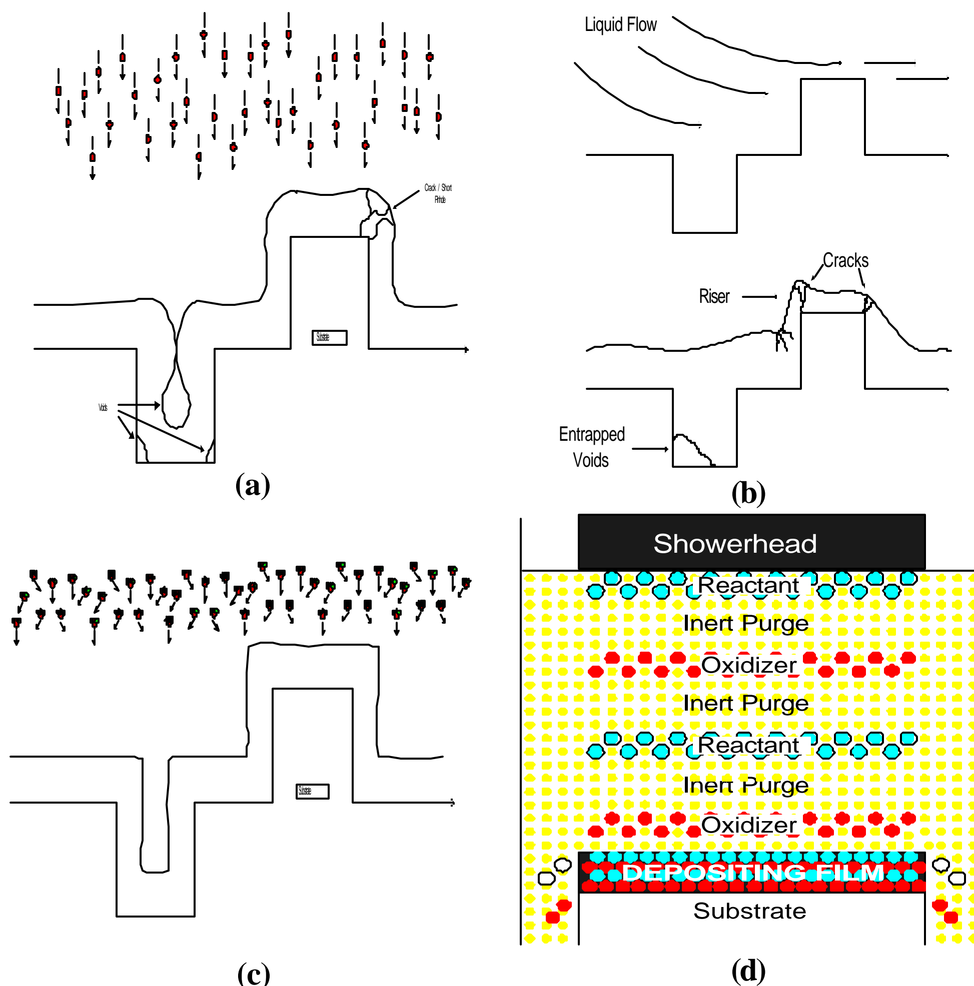

Figure 1. *Comparison of the deposition techniques. (a) MBE or PVD Deposition, (b) Spin Mist Deposition, (c) MOCVD, and (d) AL(CV)D, a form of CVD.*

In analyzing the different approaches, only MOCVD readily meets the film deposition goals of conformality, dense, pin hole free, uniform, scalability and offers a sufficient deposition rate of the thin films. Further, for complex oxides only MOCVD readily offers the ability to grade the composition. We therefore set out to develop and implement a low-temperature PZT film deposition methodology suitable for imaging and memory devices.

We use a custom *SpinCVD*™ technology to produce films. A schematic for the system is shown in Figure 2. The reactor, attached to the robotic wafer transfer cluster tool hub, is shown in figure 3. The SMI SpinCVD™ reactor is a high speed rotating disk reactor type featuring radial reactant distribution for optimum uniformity control. The reactor is designed to produce films on 6"and 8" wafers and is scalable to handle 12" wafers. The reactor has several viewports for process observation and in-situ optical process monitor access. The showerhead also offers the option to apply a plasma-enhanced mode.

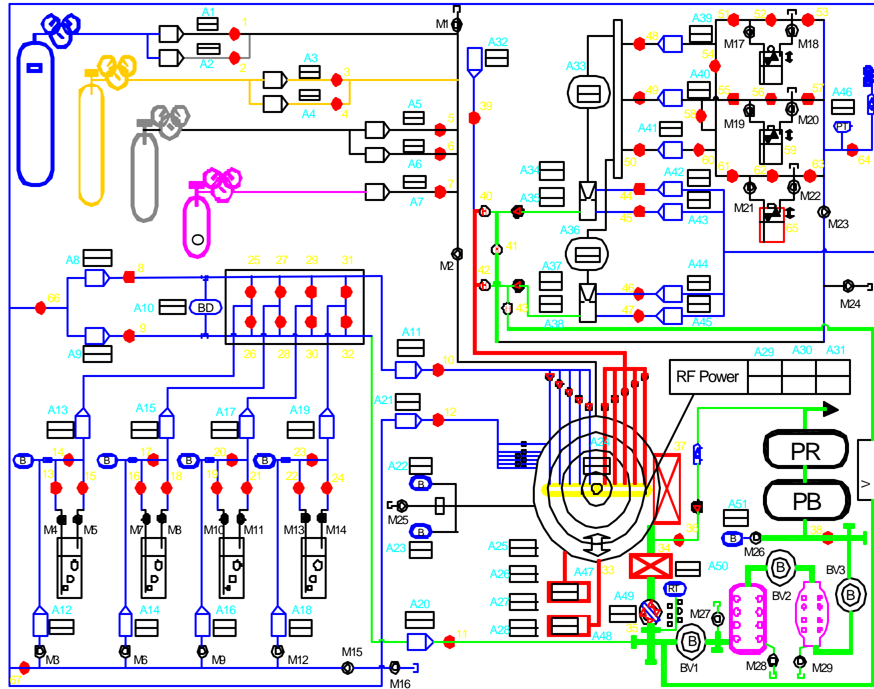

__Figure 2__. Schematic for the MOCVD reactor and gas panel developed for PZT

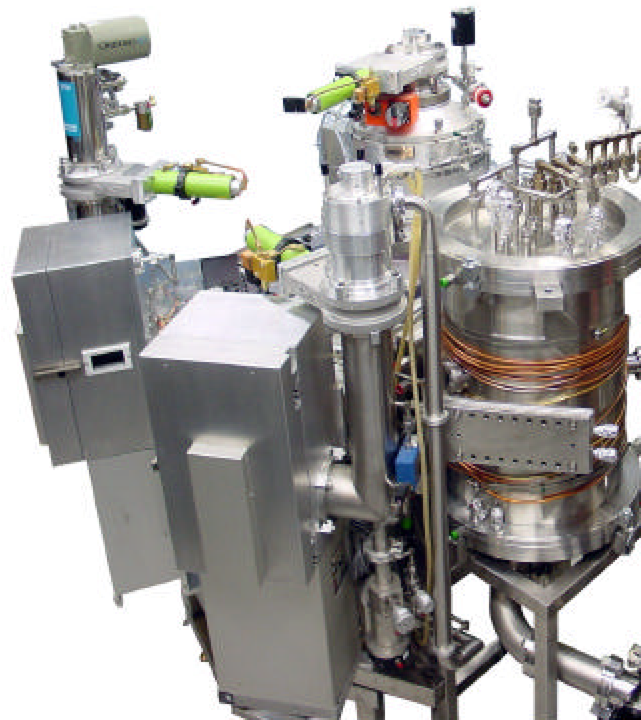

__Figure 3__ Photograph of the PZT reactor

The PZT system gas panel features include multiple liquid reservoirs from which liquid flow may be directed into flash evaporators. The precursors used for PZT growth were lead *bis*-2,6-tetramethyl-3,5-heptanedionate (thd), zirconium *bis*-thd-*bis*-*iso*-propoxide, and titanium *bis*-thd-*bis*-*iso*-propoxide. A "push" gas is used to control the flow dynamics out of the flash evaporator into either the reactor or to the vent. The flow into the reactor is segmented radially in order to control the resulting uniformity. Additionally, the precursor flow is injected within a uniform laminar flow, which maintains a state of laminar flow and thus mitigates prereactions and recirculation flows. The oxidizer is also separately introduced in order to minimize prereactions. Figure 4 shows the temperature uniformity achieved in the PZT system, and a photograph of a highly uniform 6" film produced in the system. Figure 5 shows the ferroelectric hysteresis for such a film, produced at a deposition temperature of 600°C.

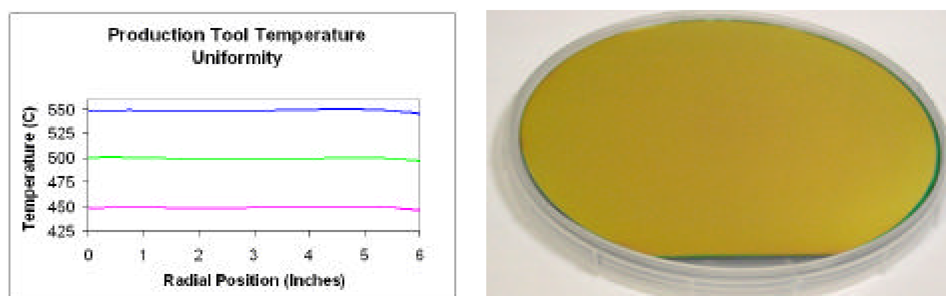

Figure 4(a). The susceptor temperature uniformity, and **(b)** photograph of highly uniform 6" PZT film.

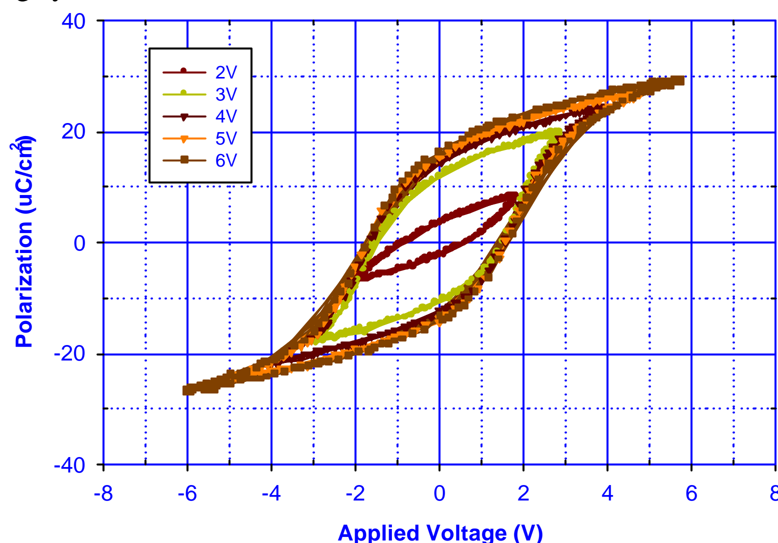

Figure 5. *Hysteresis curve of ferroelectric PZT.*

Low Temperature Deposition of PZT

Our prior work to produce PZT films for memory applications[1] achieved crystalline films with good ferroelectric behavior; but deposition temperatures at or above 550°C were required for acceptable performance. For pyroelectric device structures, lower deposition temperatures are essential to avoid exceeding the thermal budget of the preferred device structures.

We have pursued a number of strategies to decrease the PZT deposition temperature while still maintaining crystallinity. First is to optimize process parameters, particularly the oxygen partial pressure. Increasing oxygen partial pressure tends to increase the lead fraction in the films, which in turn appears to improve crystallinity. This affect of oxygen on lead deposition and the ability of lead oxide to improve crystallinity has also been observed by others.[2] Another useful approach has been to vary the concentration and solvent ratio of the precursor cocktail. We have also investigated pulsed growth, where intervals of precursor gas flow are alternated with intervals of inert gas, which has been found by others to enhance crystallinity at lower deposition temperatures. This effect has been demonstrated by Funakubo's group.[3,4,5] Films grown on a substrate with a structure similar to that of PZT's perovskite structure and with low lattice mismatch tend to be more crystalline at lower substrate temperatures, due to templating effects, than those grown on non-matched substrates;[6] we are also investigating this approach. Finally, we are currently experimenting with the addition of UV light and/or RF plasma enhancement during deposition to increase the energy of deposited species, improving atom mobility and thus crystallization kinetics.

Although these developments to reduce the crystallization temperature of PZT are still ongoing, we have succeeded in decreasing the deposition temperature at which crystallized films can be deposited by almost 100°C. Figure 5 shows x-ray diffraction (XRD) patterns of recent PZT films deposited on platinized silicon substrates at different deposition temperatures.

An interesting difference we have observed in these experiments is that the orientation of films is affected by the reduced deposition temperature: whereas previous films deposited at higher temperatures exhibited a predominant (001,100) orientation, these films increasingly show a (110,011) texture. Either orientation can be utilized for the desired application. Experiments to further reduce the crystallization temperature of PZT films are in process.

Pyroelectic results

Preliminary measurements of pyroelectric coefficients were made of several SpinCVD™ PZT films. The test conditions were: conducting oxide bottom electrode, NiCr top electrodes; the samples were poled at 150°C, 3 min., 5 – 10 V. Pyroelectric coefficients were measured at 100 Hz using the Byer-Roundy technique. The pyroelectric coefficients (p) obtained were ~20-25 nCoul/cm^2-K; however, the losses are 5-10 times higher than desirable. Inaccuracies in electrode area, due to the use of small electrode pads, may tend to inflate the apparent value of p. Thus this preliminary performance is encouraging, but more data is required to fully characterize the pyroelectric performance.

Summary

The MOCVD technology we employ, Spin CVD™, can grow high quality PZT films. Spin CVD ™ can grow films at reduced temperatures, yet of promising device quality. Thin PZT film ferroelectrics make good nonvolatile memories and thick PZT films have application as optical waveguides.

Acknowledgements

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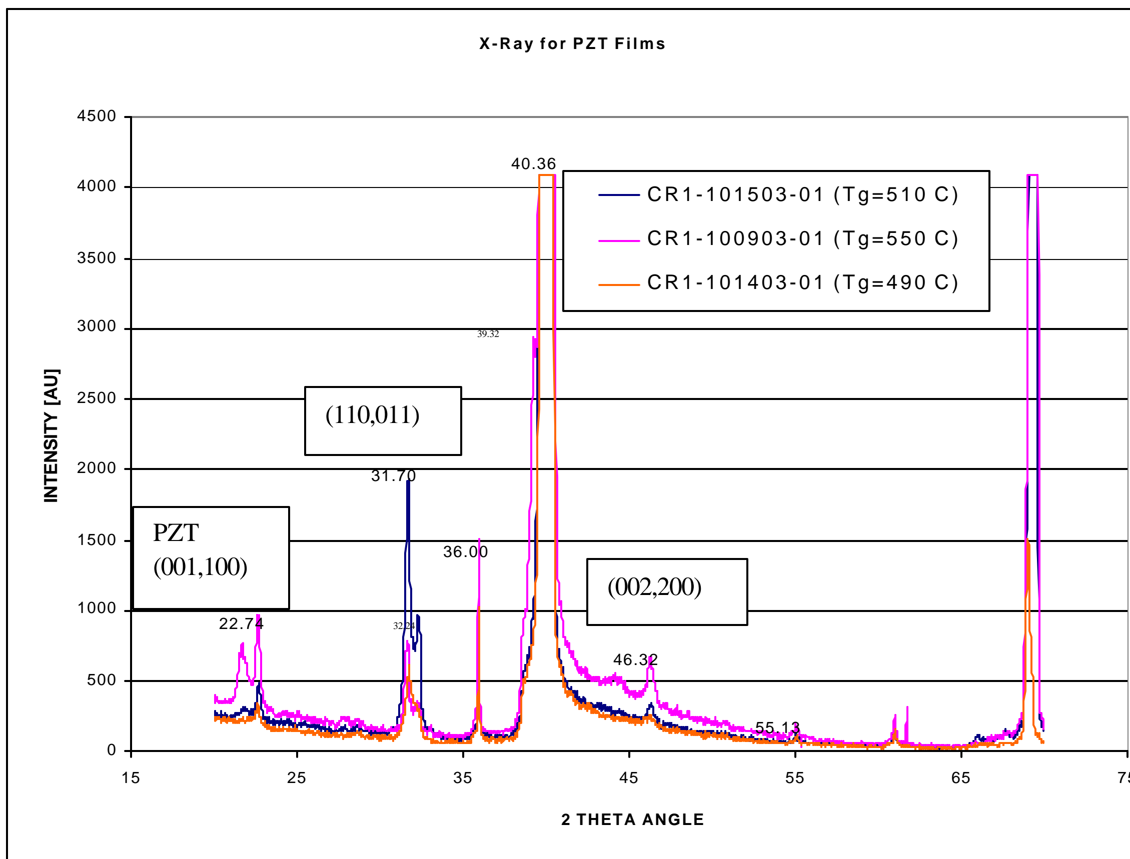

Figure 5. *XRD patterns for PZT films grown at reduced temperatures. The indicated peaks are from tetragonal PZT with an approximate Zr/Ti ratio of 30/70. The very large peaks near 40 and 70 degrees 2θ are substrate peaks.*

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