MOCVD CAPACITORS*

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DISCLAIMER

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Introduction

A significant effort within the Department of Energy's Office of Transportation Technologies and the U.S. Navy's Power Electronic Building Block (PEBB) project has focused on reducing the size and weight of power electronic devices for electric and hybrid vehicles. Power electronic circuits, which are composed of active switching elements and passive components such as capacitors and inductors, provide motor control, power distribution, and DC/AC conversion functions in electric vehicles.

Progress has been made on reducing the size and weight of power electronic components such as MOS-controlled thyristors and insulated-gate bipolar transistors. Additional effort on high-power capacitors will be needed for load leveling and filter functions. The objective of this work is to fabricate a new class of high-power capacitors with reduced size and weight. Capacitors will be integrated with semiconductor components of electric motor and actuator control subsystems.

As a subsystem component of electric and hybrid vehicles, the size, cost, and reliability of the high-power capacitor must be addressed. The PEBB project demonstrated control of three-phase and DC motors in linear actuator and valve operations.[1] The current PEBB circuitry uses large electrolytic capacitors (≈4600 μF) with large volumes (≈700 cm^3). Electrolytic capacitors are based on aluminum oxide and tantalum oxide films, which have dielectric constants of 10 and 35, respectively. The capacitance is directly proportional to the dielectric constant. Typically, perovskite-based dielectrics exhibit much higher dielectric constants than those of conventional oxide insulators (see Table 1).

Significant volume savings can be realized if high-dielectric-constant perovskite materials can be substituted for oxides with lower dielectric constants. For example, the capacitance/volume ratio of electrolytic capacitors with 1 μm-thick Al_2O_3 films is 0.009 F/cm^3. A $(BaSr)TiO_3$ (BST) film with a dielectric constant of 400 would have a capacitance/volume ratio of 0.34 F/cm^3. The actual ratio will be lower because of electrodes and external packaging. In addition, the capacitance/volume is a function of the breakdown field. The effective capacitor thickness must be increased for higher operating voltages.

Table 1. Dielectric constants of selected bulk ceramic materials[2,3,4]

Material	Dielectric Constant
Al_2O_3	10
ZrO_2	25
TiO_2	100
$Ba_{0.04}Sr_{0.96}TiO_3$	320
$Ba_{0.15}Sr_{0.85}TiO_3$	400
$Ba_{0.40}Sr_{0.60}TiO_3$	880
$PbZr_{0.53}Ti_{0.47}O_3$	820

Argonne National Laboratory has extensive expertise in the fabrication and characterization of perovskite thin films by metal organic chemical vapor deposition (MOCVD) and has extended this capability to develop volume-efficient capacitors.[5-8] The MOCVD synthesis technique, which is widely used in semiconductor manufacturing, is a method for depositing uniform layers of material over a large surface area. Much of this technology can be adapted for the development of high-power capacitors for the automotive industry.

Procedure

Fabrication of an MOCVD system requires five main subsystems (Figure 1). First, reservoirs are required to contain the chemical precursors and the carrier gases. Second, a vapor delivery and mixing system is needed to transport the chemical vapors from their reservoirs and appropriately mix the reactants when necessary. Third, a quartz deposition chamber (reactor) is used to grow the films; the reactants are injected into this chamber via the piping network and controllably reacted to produce the desired film. The reactor, typically equipped to control the total reactor pressure and the deposition temperature at the substrate surface, is designed to produce a uniform and stable flow profile of the reactant past the substrate surface. Fourth, a pumping system is required to remove the exhaust gases from the deposition chamber. Fifth, a chemical scrubbing system treats the exhaust gases.

Currently, ANL operates three MOCVD systems. Two of the reactors are devoted $Pb(Zr,Ti)O_3$ (PZT) deposition; the third has been modified to include a liquid delivery system for deposition of BST.

Prototype capacitors consist of a layered conductor/dielectric structure on a silicon substrate. Ruthenium oxide or platinum-base electrodes are first deposited on the silicon substrate. The dielectric layer (PZT or BST) is deposited on the bottom electrode by MOCVD. The top (silver) electrode is deposited on the dielectric by electron-beam evaporation. Electrical characterization of the capacitors includes determination of dielectric constant and loss, leakage current, and dielectric breakdown strength.

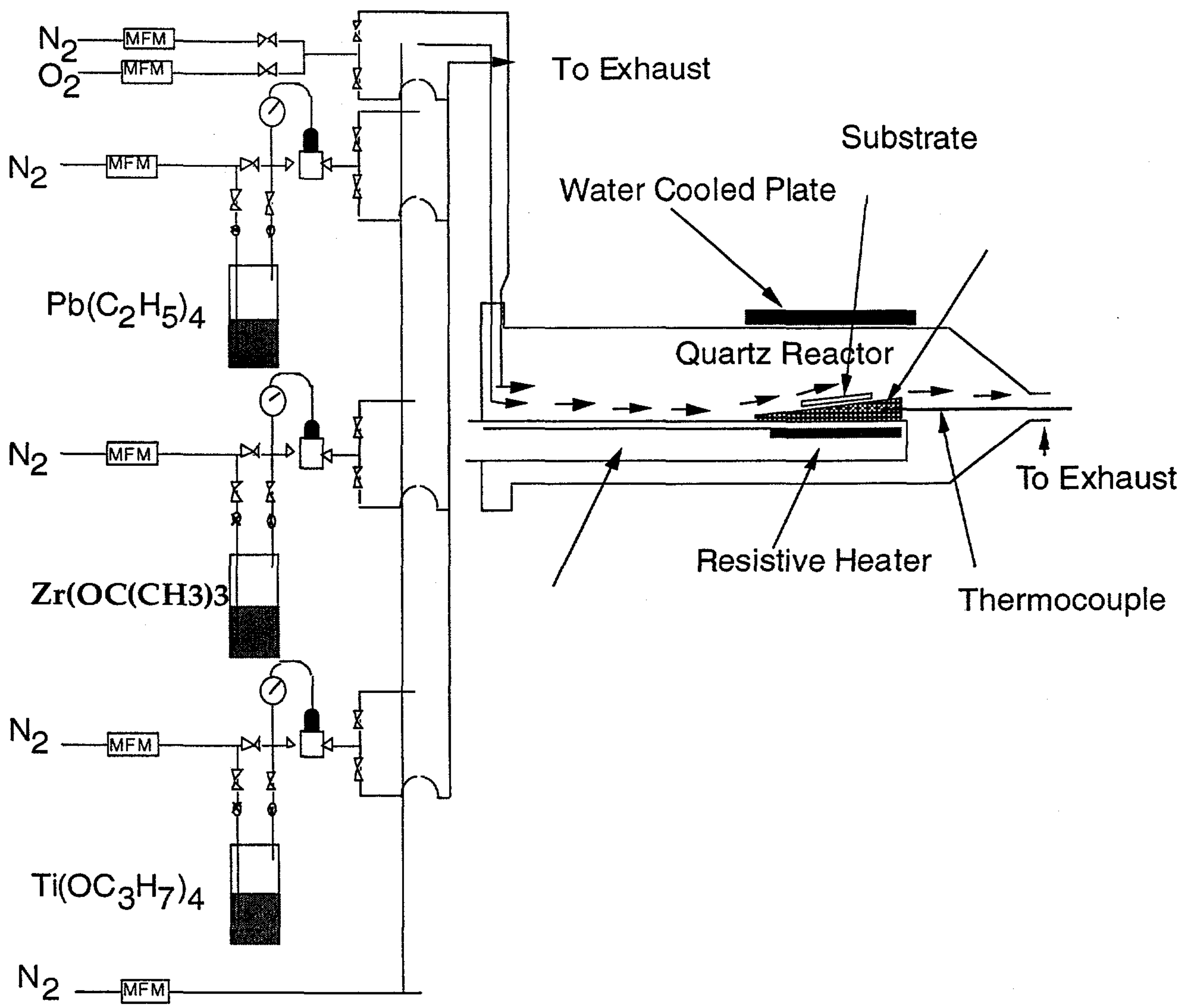

Figure 1. MOCVD system for deposition of $Pb(ZrTi)O_3$.

Results

Our approach to this project consists of four parts: (a) synthesis and processing of high-dielectric-constant films by MOCVD, (b) evaluation of the electrical properties of model capacitors, (c) design of ceramic-thin-film-based capacitors for automotive applications, and (d) collaboration with an industrial partner to integrate and scale up the MOCVD process.

We have established an approach to develop and evaluate PZT- and BST-based materials for power electronic applications, focusing on a range of compositions to optimize dielectric properties. Ferroelectric materials, such as BST or PZT exhibit have high dielectric constants that can be controlled by composition of either the A- or B-site cations. Film growth conditions were optimized by controlling vapor pressure and gas flow of the independent Pb, Ti, and Zr sources. The substrate temperature was between 450 and 550°C. Film stoichiometry was monitored by X-ray fluorescence, and phase development was confirmed by X-ray diffraction (XRD). Figure 2 shows that the perovskite phase can be formed in PZT films.

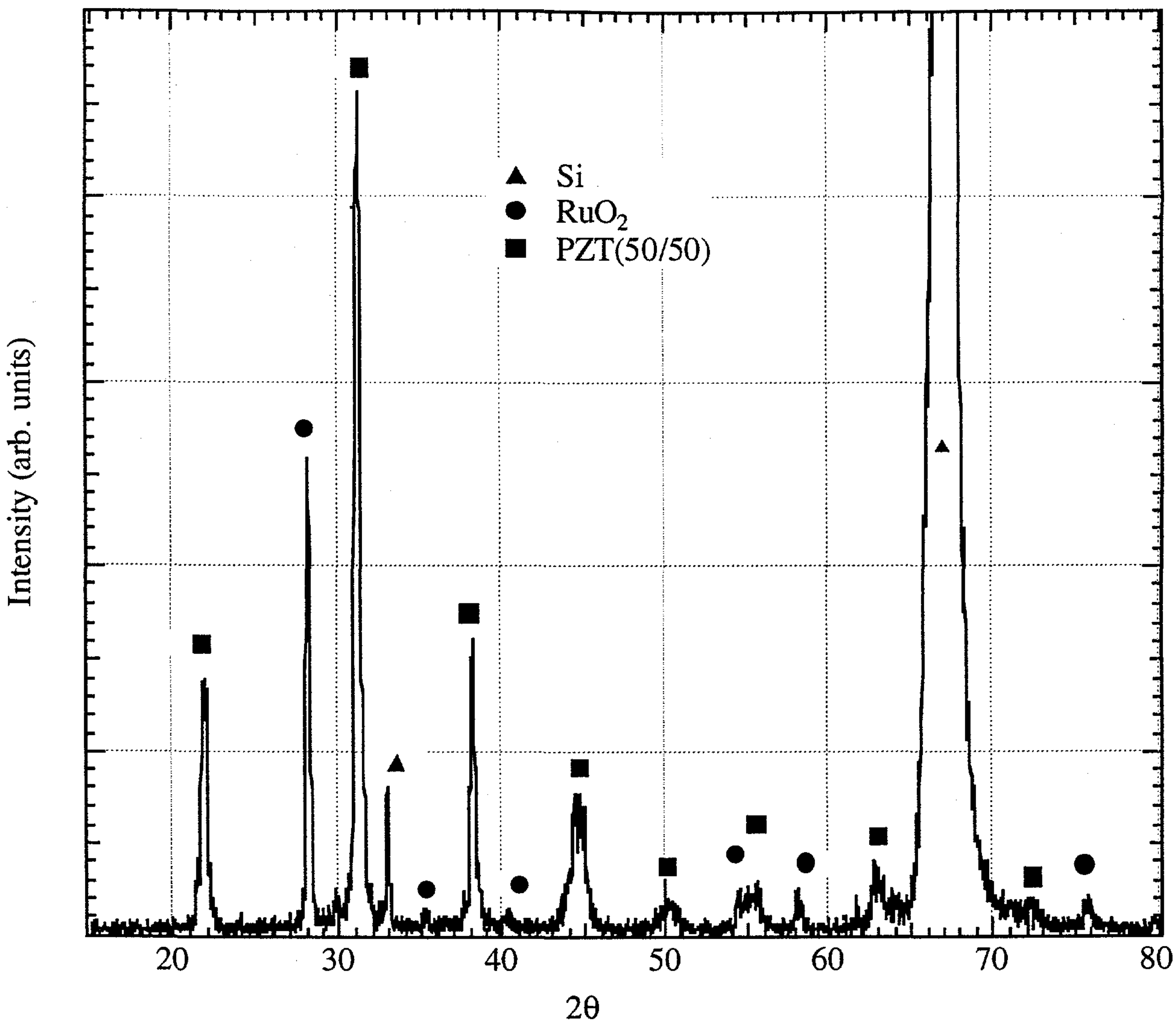

Figure 2. XRD pattern showing a phase-pure perovskite.

PZT-based capacitors were fabricated on silicon substrates and were tested for dielectric constant and loss. The top silver electrode was patterned with various diameter pads (0.75, 0.25, 0.1, and 0.05 mm diameters) to test dielectric uniformity. The dielectric constant ranged between 330 and 500 for films that were 0.5 μm thick, whereas dielectric loss ranged from 0.01 to 0.03. Dielectric-film uniformity was characterized on capacitor structures by measuring the dielectric properties of 0.75-mm-diameter capacitors over the entire film. An average of 30 pads were measured for each sample. Several of the samples showed no shorting over areas of 0.5 cm^2, which yields capacitance/area ratio of 1 $\mu F/cm^2$. Future work will be devoted toward increasing defect-free capacitor area and exploring the nature of the defects that cause shorts in the capacitors.

The successful development of ceramic-thin-film-based capacitors requires further materials improvements in the areas of dielectric constant, leakage current, and dielectric breakdown strength. During operation, large electric fields occur in the dielectric layers of capacitors of this type. These electric fields can cause dielectric breakdown and limit component reliability. In collaborative work with Hewlett Packard, we measured the properties of 2000-Å-thick BST films that exhibit a dielectric constant of 320 and found that they will require high breakdown strength for high-voltage applications. These BST films have already demonstrated a dielectric breakdown strength of 3 x 10^8 V/m, which is high enough to support many high-voltage capacitor applications.

Design of Ceramic-Thin-Film-Based Capacitors for Automotive Applications

One advantage of MOCVD over other deposition methods is its superior infiltration, which allows uniform coating of large areas and complex surface geometries (e.g., step coverage via filling, and high-aspect-ratio trenches). Energy storage capacity may be increased by depositing dielectric films on grooved silicon substrates, which have greater surface areas. Recent work at Siemens has demonstrated that high-surface-area films can be deposited on etched Si wafers. The surface area is increased 85 times by etching.[8] The MOCVD process is ideal for coating these complex shapes.

Specific designs for ceramic-thin-film-based capacitors will be based on prior development work. Other design criteria will focus on component reliability and on the tailoring of conductive paths to maximize peak power output. Component reliability will be tested in two ways. First, the electrical behavior will be measured over a specified number of charge/discharge cycles. Second, mechanical reliability will be explored by shock testing and mechanical fatigue experiments.

Summary

Many perovskite materials exhibit a highly nonlinear dielectric response, which leads to a very high effective dielectric constant; these materials offer enhanced capacitance in smaller volumes. Prototype capacitors that we fabricated on planar silicon substrates exhibited high dielectric constants. To scale up and design larger capacitors, we must be able to coat complex shapes and minimize defects in the dielectric films.

Acknowledgment

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