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A Comparison of the Properties of Candidate Ferroelectric Films for Non Volatile Memories

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A comparison is made of two material families which are candidates for ferroelectric nonvolatile memories. The materials are $Pb(Zr_xTi_{1-x})O_3$ (PZT) and $Sr_{1-x}Bi_{2+y}Ta_2O_9$ (SBT). Properties of representative structures produced at NCSU and other laboratories are presented and compared. It is emphasized that properties are strongly dependent upon substrates, electrodes, microstructures and compositions. General comments are also made regarding process temperatures and other integration issues.

1. INTRODUCTION

There is presently a substantial effort underway to commercialize ferroelectric nonvolatile memories (FRAMs), using ferroelectric thin films as the bit-cell capacitors. The leading most studied candidate material has been the $PbZrO_3$-$PbTiO_3$(PZT) solid solution family. More recently there has been study of a promising new candidate *viz.* $SrBi_2Ta_2O_9$, and analogues such as $SrBi_2Nb_2O_9$.

In this paper a brief review is presented of properties and important issues related to these materials.

2. PROCESSING AND PROPERTIES OF PZT

A number of techniques have been successfully utilized to prepare PZT thin films, including ion beam sputter deposition (IBSD);[1,2] DC and RF magnetron sputtering;[3,4] pulsed laser ablation deposition (PLD);[5,6] chemical vapor deposition (MOCVD),[7,8] sol-gel,[9,10] metalorganic decomposition (MOD), and other methods. The process methodology has advanced to the point that all of the listed methods can produce ferroelectric films with acceptable properties, as summarized in Table I. However, not all of the methods appear suitable for integration with silicon semiconductors fabrication, and MOCVD and sol-gel are leading candidates. Several groups have demonstrated PZT film CVD on 6-inch wafers.[11]

The data included in Table I is for PZT with a range of Zr/Ti ratios. For bulk polycrystalline ceramics, properties display a sharp maximum near the 53/47 morphotropic phase boundary. This effect is less marked in thin films; in fact various groups prefer Zr-rich compositions (lower switching fields, rhombohedral symmetry); Ti-rich compositions (larger Pr, tetragonal symmetry); or phase boundary compositions (larger ε). The optimum is dependent upon process method and electrode/substrate selection. However, there is another important implication, namely that tight control of the Zr:Ti stoichiometry ratio is not critical in an integrated process.

It has been shown that the high volatility of PbO at elevated temperatures can be used to advantage. While the sticking coefficient of Pb reduces markedly at substrate temperatures over 500°C, conditions can be found which yields a "self-limiting" control of Pb content in the perovskite. Altogether, these factors make control of PZT composition simpler than other systems.

In early years, synthesis of PZT thin films was plagued by the occurrence of an unwanted fluorite (pyrochlore-type) phase. A number of strategies have been developed to deal with this issue. For vapor deposited films, these generally involve control of the film nucleation step.[12] for sol-gel processes, one can also modify the sol-gel chemistry.[13]

Table I. Representative Properties of PZT Films by Various Process Methods

Process Method	2 Pr ($\mu C/cm^2$)	$P_{sw} - P_{ns}$[1] ($\mu C/cm^2$)	Permittivity ε[2]	Ec (kV/cm)	%Fatigue @cycles	Substrate	Film thick. (nm)	Ref.
Sputtering (RF magnetron)	80	-	400	28	<2%@10^{12}	Pt/MgO	?	3
Ion Beam Sputtering (IBSD)	60	~40	-	<100	7%@10^{11}	Hybrid on MgO	180	1,2
MOCVD	40	23	-	50	66%@10^{11}	Pt/Si	~200	7,8
PLD	60	15	-	30	0%@10^{11}	LSC/MgO	380	5,6
Sol-gel	90	50	-	45	0%@10^{11}	Hybrid on MgO	180	19

1. Dependent on measurement method. Some measurements P*-P^ on RT-66A.
2. Usually low field measurements.
3. "Effective" value as measured by RT-66A at the saturation field, if quoted.
4. The data for MOCVD is for fully integrated and backend processed structures. Properties are better for simple capacitor

Table II Representative Properties of PZT Films withVarious Electrodes and Substrates

Electrode Type	2Pr ($\mu C/cm^2$)	P_{sw}-P_{ns} [1] ($\mu C/cm^2$)	% Fatigue @ cycles	Resistivity (Ωcm) [2]	Zr/Ti	Ref.
$Pt/SiO_2/Si$	30	20	>90%@10^{11}	>10^{10}	53/47	16
Pt/MgO	60	45	50%@10^{11}	>10^{10}	53/47	10,15
RuO_2/MgO	55	18	0%@10^{11}	10^6-10^8 [3]	53/47	15
RuO_2/Si	30	20	0%@10^{11}	10^6-10^8 [3]	53/47	16
LSCO/Pt/ BTO/Si	18	12	0%@10^{11}	10^{10}	20/80	27
Pt/IrO_2	33	-	0%@10^{12}	-	52/48	28
Hybrid Pt/RuO_2	90	50	0%@10^{11}	10^9	53/47	19
Cosputtered Pt/RuO_2	85	60	20%@10^{11}	~10^8	53/47	19

1. Pr* - Pr^ from RT-66A.
2. Effective resistivity as measured at high field on RT-66A.
3. Very dependent on process conditions.

Research on PZT film capacitors has made it clear that the electrodes have a major influence on properties, both directly and indirectly. This is partly demonstrated in Table II, which shows properties of PZT films with a variety of electrode/substrate combinations. This was first realized in terms of fatigue, where it was shown that PZT on oxide electrodes typically display superior resistance to polarization fatigue than PZT films on Pt electrodes.[14-17] The situation is more than simply an issue of electrode type, however, as careful control of film orientation and microstructure on Pt electrodes can allow acceptable fatigue. Conversely fatigue can also be observed for PZT with oxide electrodes under certain conditions.

Because films nucleate and grow on the electrodes, the electrodes have been shown to have a substantial effect on the microstructure.[16,18] control of microstructure and properties has also been achieved via the use of "hybrid" electrodes.[19,20] For example, we have shown that thin Pt layers on RuO2 allow one to control film nucleation, control the Schottky barrier, and obtain large values of remanent polarization without compromising fatigue performance. Other variations have been explored, including co-sputtered Pt and RuO_2.[19,20] The attractive properties which can be achieved can be seen in Table II.

3. PROCESSING AND PROPERTIES OF SBT

$SrBi_2Ta_2O_9$ is one of a family of layered perovskites, the ferroelectric nature of which have been known for some time.[21] Thin films of these materials have only been explored much more recently.[22] In comparisonn with PZT, only a limited number of process methods have been applied to the film growth of SBT, *viz.* sol-gel and PLD, 23-26) similarly, substantially less is known about the processing-microstructure-property relationships for the material. However, the films display considerable promise, as they have acceptable values of Pr and switched-non-switched polarization, low coercive fields, low leakage, and do not appear to display significant fatigue when used in conjunction with Pt electrodes. (See Table III).

One must be cautious with the assumption of 1::2:2:9 stoichiometry. The properties are known to be strongly dependent upon composition, and it is believed that the optimum properties are achieved for compositions which are Sr-deficient and Bi-rich compared to the nominal SrBi2Ta2O9. The exact relationships have not been published.

The major drawback of the material at the present time is the high process temperatures which are required. These are typically in the range 750-800°C, which presents a problem for integration as discussed below.

Table III Representative Properties of SBT Sol-gel Films

2Pr ($\mu C/cm^2$)	Psw-Pns ($\mu C/cm^2$)	Fatigue, %@ cycles	Ec (kV/cm)	Thickness (nm)	Ref.
13.2	7.5	~15% @10^{12}	55	200	23
37	29	<5%@10^{10}	~48	280	24
20	-	0%@10^{11}	35	240	25

4. COMPARATIVE COMMENTS AND INTEGRATION ISSUES

Both PZT and SBT families have a set of advantages as well as disadvantages as they are considered for commercialization in FRAMs. In terms of properties, SBT was initially considered to have a rather low value of switched-non switched polarization for high density devices. However, the values quoted recently for 2Pr are encouraging, 24,25) and are in fact almost twice the literature value for bulk materials. However, composition and orientation issues must still be elucidated. On the other hand, careful choice of PZT composition, electrode system, and process conditions can yield excellent materials, with very large switched minus unswitched polarizations, coercive voltages of ~1 V, operation as <3 V, and excellent fatigue and imprint resistance.

Considering processing issues, the presence of Pb in PZT is extremely unattractive in a semiconductor lab. However, it does allow processing at temperatures below 550°C. In contrast, SBT at present requires a much greater thermal budget, for example 800°C for > 20 minutes. This is a severe problem if high density devices are contemplated, where the bottom electrode must be contacted down to an underlying plug. To date conductive thermal barriers capable of surviving this processing thermal budget under moderately oxidizing conditions have not been identified.

There are many other integration issues which are presently being addressed, including backend processing, compatible dielectrics, passivation barriers, reproducibility and process window, breakdown mechanisms, imprint, *etc.*

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