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Maria Huffman
Ramtron International Corporation, Colorado

Mowafak M. Al-Jassim
National Renewable Energy Laboratory, Colorado

Chuck Echer
Lawrence Berkeley Lab., California

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TRANSMISSION ELECTRON MICROSCOPY AND NANOPROBE ANALYSIS OF FERROELECTRIC THIN FILMS

Maria Huffman*, Mowafak M. Al-Jassim[1], Chuck Echer[2]

Ramtron International Corporation, Colorado Springs, CO 80921
[1]National Renewable Energy Laboratory, Golden, CO 80401
[2]National Center for Electron Microscopy, Lawrence Berkeley Lab. (Bl. 72/211), Berkeley, CA 94720

Abstract

Thin-film ceramic materials have a variety of electronic applications. Several deposition techniques are currently being used to produce such films with specific properties. For example, rf-sputtered ferroelectric perovskite films, with total thicknesses less than 0.5 μm, are being integrated with semiconductor devices as elements for non-volatile memories. Since there is a definite need to characterize these thin films after deposition, electron microscopy has been utilized as one of the most powerful techniques available for examining their morphology and microstructure. Transmission electron microscopy (TEM) examination of these oxides proved difficult. New TEM sample preparation techniques had to be developed in order to avoid artifacts. Ion milling had to be kept to a minimum because many ferroelectric materials contain lead or other volatile elements. Even though milling has worked quite well under certain conditions, other techniques, such as microtoming, have been successfully used by the authors. In this work, both kinds of sample preparation are explored and compared. Particular emphasis is placed on the understanding of the compositional and microstructural variability of these films, as they are integrated in semiconductor devices.

Key Words: Ferroelectrics, thin films, oxide ceramics, transmission electron microscopy, sample preparation techniques.

*Address for correspondence and present address:
Maria Huffman,
Symetrix
5055 Mark Babling Blvd.
Colorado Springs, CO 80918
Phone No.: (719) 594 6145
FAX No.: (719) 598 3437

Introduction

Thin-film oxide ceramic materials are presently receiving much attention. Thin ferroelectric films are currently being integrated in semiconductor memories as non-volatile elements or as high dielectric constant materials replacing SiO_2, Ta_2O_5 in high density dynamic random access memory chips (Evans and Womack, 1988; Bondurant and Gnadinger, 1989; Moazzami *et al.*, 1990; Dey *et al.*, 1991). Full characterization of these films before and after processing is imperative because they tend to be very sensitive to annealing times, ambients and temperatures, to plasma environments, and to chemical etching.

Electron microscopy techniques are very valuable characterization tools for understanding the morphology and microstructure of these oxide ceramic systems, and, coupled with other thin film compositional techniques, information can be obtained that can then be used for semiconductor process improvements (Kirk *et al.*, 1989; Anderson *et al.*, 1989, 1992). Many of these ferroelectric materials are not only oxides that can have stoichiometry control issues but also contain very volatile components, such as lead, which make both sample preparation and compositional analysis quite difficult (Reaney and Barber, 1990).

In this paper, we describe the preparation and transmission electron microscopy (TEM) examination of various ferroelectric thin films. Due to the sensitivity of these films to ion and electron beams, particular care was taken during the preparation and examination of these materials.

Materials and Methods

The materials investigated in this paper are thin-film, lead zirconate titanate (PZT) ceramics deposited by either rf-sputtering or by sol-gel techniques. The thickness of the films analyzed varied between 0.2-0.4 μm. The composition of the films is titanium-rich, ranging from $Pb_{1.0}(Zr_{0.48}Ti_{0.52})O_3$ to $Pb_{1.0}(Zr_{0.30}Ti_{0.70})O_3$ Dopants such as La and Ca have also been used to modify the electrical properties of these films (Huffman

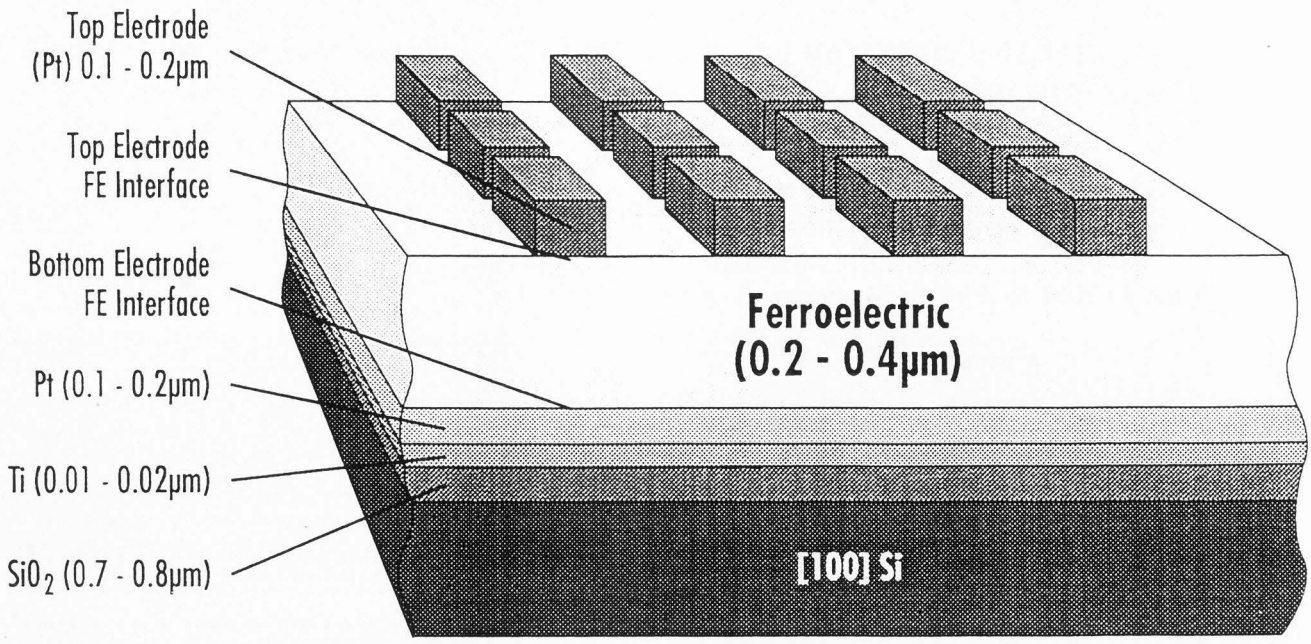

Figure 1. Simple test structure used for electron microscopic evaluation. There are variable sizes of the top electrode. Electrical characterization can also be performed on this structure.

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and Schuele, 1993; Huffman *et al.*, 1993). The substrates are [100] Si, followed by a 0.7-0.8 μm SiO_2 layer that may be boron and/or phosphorus-doped or undoped. The bottom electrode structure consists of a thin Ti layer (0.01-0.02 μm) followed by Pt (0.1-0.2 μm). To prepare capacitor structures for memories, not only is a top electrode structure necessary (usually Pt), but several other layers (glass, metallization, passivation, etc.) are applied in order to finish the device structure. Most of our work has been focused on simple test structures (Figure 1).

The samples used in this work were characterized electrically. This served as a selection criterion for TEM examination and also for correlating the electrical properties with the structural and morphological properties of the films. TEM and analytical electron microscopy examinations were performed using a Philips CM30 microscope, operating at -300 kV, and a JEOL JEM 200CX AEM, operating at 200 kV. The 200CX is equipped with a KEVEX System 8000 and two X-ray detectors: (**1**) a high-angle energy dispersive spectroscopy (EDS) detector and (**2**) an ultra-thin-window EDS detector for light elements (Z = 6 and up). Further, hot stage work has been done using a tantalum, heated Gatan 628-Ta specimen holder. The liquid nitrogen work has been performed using a cryogenic Gatan 636 specimen holder. The CM30 is also equipped with a Kevex system and an EDS detector, and it has been used for some of the analytical work. The samples used for the TEM work are wafer pieces that are first mechanically polished and dimpled to a thickness of less than 20 μm before ion milling. A variety of milling conditions have been tried. Milling angles of 12°-16° and milling times between 20 and 40 minutes have been used. The beam current was in the 20-30 μA range, while the accelerating voltage was between 3-4.5 keV. Milling was performed at both room and liquid nitrogen temperatures to investigate the dependence of Pb content on sample preparation. No significant changes have been observed in the appearance of the films. The sputtering rates of the various components in PZT differ appreciably from each other, and it is possible that any kind of sample preparation process that involves sputtering will cause some degradation or artifacts. Both plan-view and cross-sectional samples were prepared.

In addition to the above-mentioned sample preparation technique, cross-sections were prepared using ultramicrotomy (Malis and Steele, 1990). In this method, 1 x 1 mm wafer pieces were embedded in epoxy. It is important at this stage to avoid the trapping of air bubbles in the epoxy. Subsequently, the embedded samples were mounted on the stage of a Reichert Ultracut S microtome system. Sections having a thickness of 0.05 μm were made using a diamond knife. Glass knives were avoided after initial trials due to their insufficient hardness.

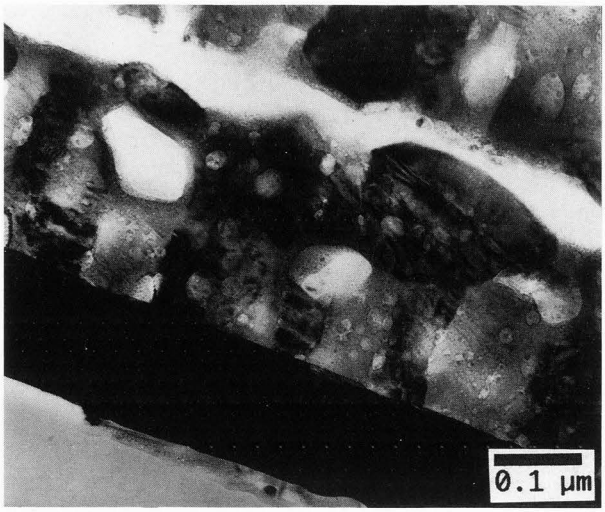

Figure 2. Cross-sectional view of an undoped, rf-sputtered PZT thin-film sample ($Pb_{1.0}(Zr_{0.48}Ti_{0.52})O_3$) that was prepared by ion milling.

Results and Discussion

TEM examination of the as-deposited films revealed that they were amorphous. To obtain the desired perovskite, ferroelectric structure, ex-situ annealing in oxygen is performed at temperatures ranging from 550°C to 850°C in either a furnace or an RTA (Rapid Thermal Annealing) environment. Films having a titanium-rich composition are tetragonal and ferroelectric (Jaffe *et al.*, 1971). Upon reaching the Curie temperature, a transition from tetragonal to a cubic and paraelectric phase is observed. The samples in this paper have Curie temperatures between 275° and 425°C depending on composition and dopant levels (Jaffe *et al.*, 1971; Huffman *et al.*, 1993). X-ray diffraction is routinely performed on the thin film samples to check their phase purity (Roy and Etzold, 1992; Huffman *et al.*, 1993). After annealing, the perovskite phase is predominant.

For plan-view examination, the easiest way to minimize sample preparation is to deposit the ferroelectric film on an electrode structure without the Ti adhesion layer (Figure 1), as Pt does not adhere to SiO_2. Thus, when wafers are cleaved, the Pt/ferroelectric film can be peeled from the substrate. This film requires minimal milling because it is only about 0.6 μm or less in thickness. If this technique is not employed, wafer pieces are milled from the Si substrate side after they have been mechanically thinned and dimpled.

Figure 2 shows a cross-sectional micrograph of an rf-sputtered PZT film with composition $Pb_{1.0}(Zr_{0.48}Ti_{0.52})O_3$. Care must be taken in preparing cross-sections because the films are under considerable tensile stress. When wafer pieces are cleaved, or during the mechanical thinning process, the samples may come apart at the bottom electrode/PZT interface. It is well known that ion bombardment modifies the sample surface and can also cause surface roughening. The various changes that occur during the milling process have been extensively documented in the literature (Auciello and Kelly, 1984). The sample in Figure 2 has been thinned by ion-milling. The milling rates of the individual layers in the structure shown in Figure 1 are very different, so very low milling angles are necessary to avoid complete removal of the ferroelectric layer. Even though we have been able to obtain quite reproducible results by ion milling (Huffman *et al.*, 1993), Figure 3 shows a series of cross-sections of a La-doped PZT sample (PLZT) ($Pb_{0.97}La_{0.03}(Zr_{0.30}Ti_{0.70})O_3$) that were prepared by ultramicrotomy. This sample preparation technique can cause certain well documented artifacts, such as sample fracture, plastic deformation, knife marks, and others (Malis and Steele, 1990, 1992; Popoola *et al.*, 1992). However, the ease of obtaining the cross-sections illustrated in Figure 3 is significant compared to the effort needed with ion milling. Figure 3a shows the columnar nature of the PLZT film with the Pt electrode intact. In Figure 3b, the electrode was not present (fell away during sectioning), but still the PLZT layer is intact through the whole film thickness. Figures 3c and 3d show higher magnification micrographs of PLZT grains. Figure 3d illustrates that sectioning has affected the integrity of this particular cross-section by the wide boundary between the two grains that are almost coming apart. In both Figures 2 and 3, the overall sample morphology is similar.

There are two interesting features in these films. They are quite columnar (as is the Pt electrode structure under the ferroelectric), and they have a high density of micropores. Plan-view micrographs show the microporosity of these films rather well. Figure 4 shows bright field micrographs of various, rf-sputtered films. The amount of microporosity in the films, either at the grain boundaries or within the grains, and the grain size vary significantly. As both ion-milled and ultramicrotomed samples show these features, they cannot be artifacts. This porosity affects film properties (Huffman and Schuele, 1993), and the best electrical results are obtained on samples with very low density of micropores. These pores vary in size from under 0.01 μm (Figure 4b) to a few hundred A in a few cases (Figures 4c and d). We believe that these pores are created during the annealing of the films (Huffman *et al.*, 1990;

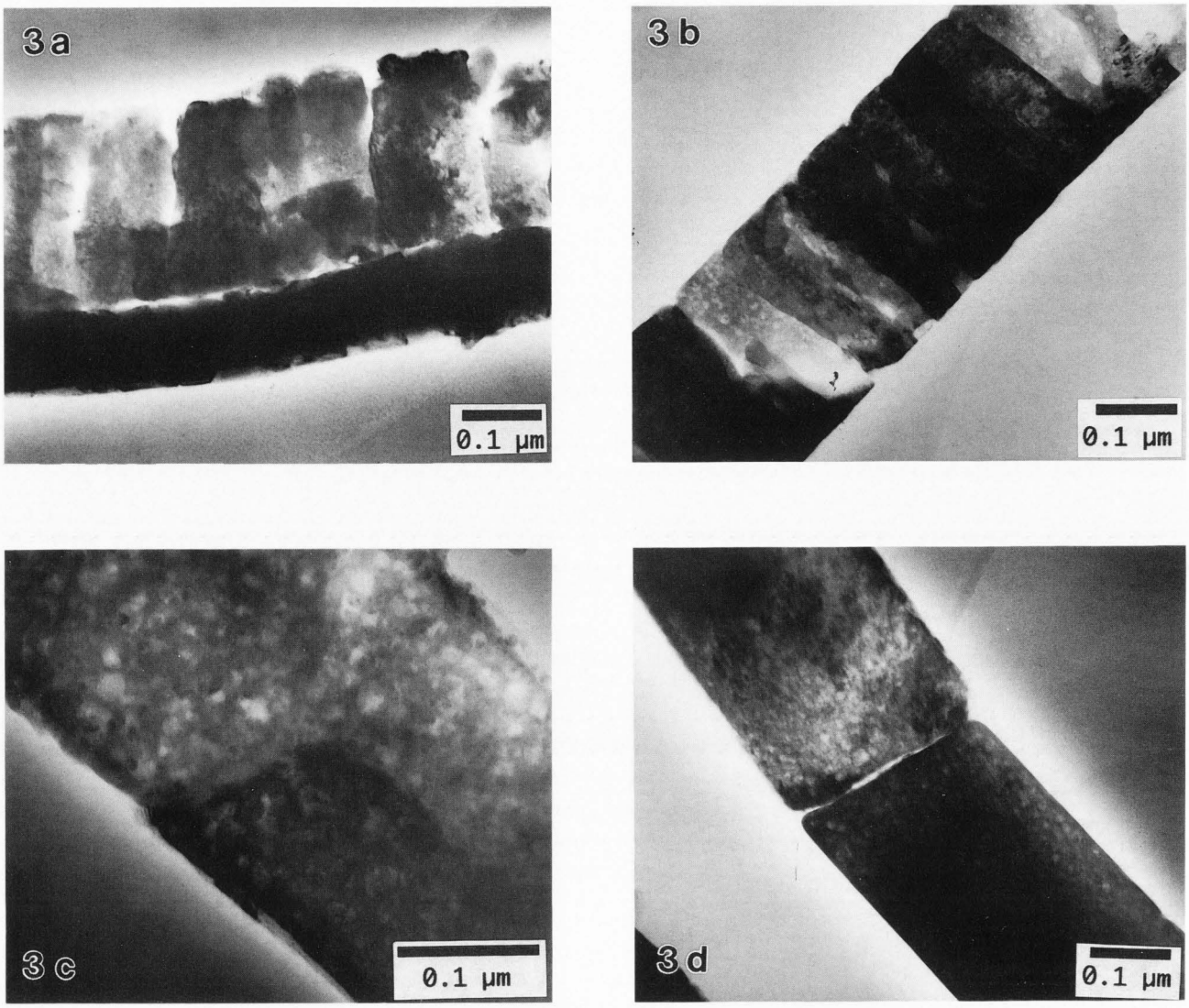

Figure 3. Series of cross-sectional views of a La-doped, rf-sputtered PZT thin-film sample (PLZT) ($Pb_{0.97}La_{0.03}(Zr_{0.30}Ti_{0.70})O_3$) that was prepared by ultramicrotomy. In (**a**) the platinum bottom electrode is visible but in (**b**), (**c**), and (**d**) only the PLZT film is shown.

Goral *et al.*, 1990). Since excess Pb is used in the sputtering targets, it is possible that these pores are created after Pb-rich phases have been driven off the samples by annealing, which is usually done at temperatures higher than 500°C. Other authors (Kwok and Desu, 1992) have proposed that these film features are not pores but simply thinner areas in the samples. In any case, they are still correlated to annealing temperature. We have shown (Huffman *et al.*, 1992b) that pore-free films can be produced given the appropriate processing conditions.

Another very important feature of ferroelectric materials is domain structure (Jaffe *et al.*, 1971; Lines and Glass, 1977). Since ferroelectric materials are polarizable and they can keep a stable polarization state even after the effect of an electric field is removed, the analysis of domains is of utmost importance. In bulk ceramics, the grain sizes are quite large (on the order of several micrometers). In the thin-film regime, the grain size is usually sub-micrometer. In these ceramic materials, domains occur as {110}-type lamellar microtwins (Lucuta *et al.*, 1985; Goo *et al.*, 1980; Randall *et al.*, 1987; Lucuta, 1989; Goral *et al.*, 1990). Figure 5 shows a sol-gel deposited, La-doped ferroelectric film

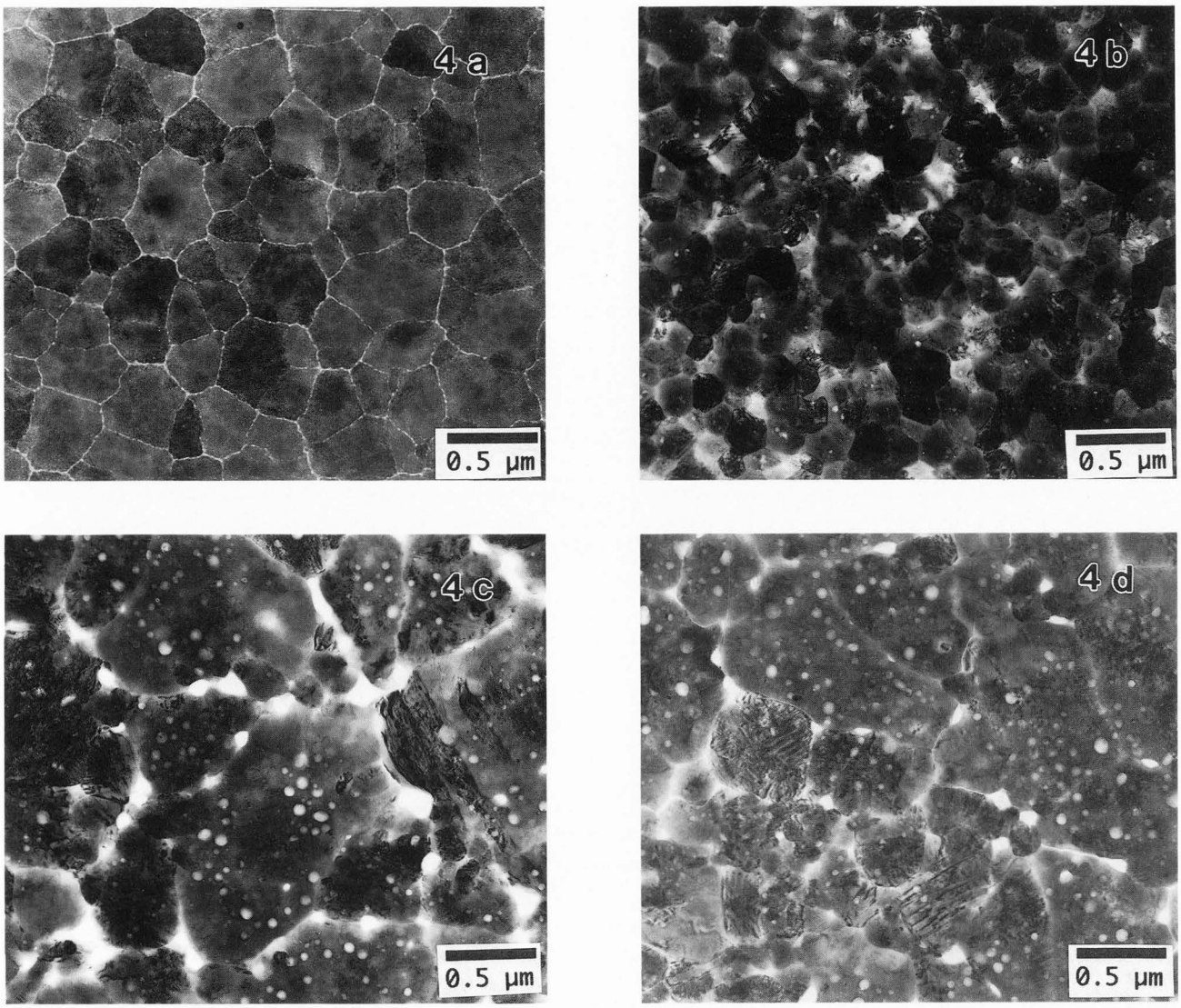

Figure 4. Bright field transmission electron micrographs of various rf-sputtered PZT films showing different morphologies. To date, the best electrical properties are obtained from films with the general microstructure shown in (b). (**a**) $Pb_{1.0}(Zr_{0.48}Ti_{0.52})O_3$; (**b**) same composition as (a) but different deposition system; (**c**) and (**d**) $Pb_{0.85}Ca_{0.15}(Zr_{0.30}Ti_{0.70})O_3$. Deposition system same as in (a).

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of composition $Pb_{0.97}La_{0.03}(Zr_{0.30}\ Ti_{0.70})O_3$. The domains are clearly visible, and Figure 5a shows a room temperature micrograph whereas Figure 5b shows the degradation of the domain structure after an in-situ hot-stage TEM heating cycle up to 300°C. As we have seen before (Huffman *et al.*, 1992a), this degradation is a combination of electron beam-sample interaction and temperature. Since the twinning occurs to relieve stress from the cubic paraelectric phase to the tetragonal ferroelectric phase in these samples, the distortion associated with this transition is very small [about 1.03 c/a close to the 48/52 Zr/Ti ratio (Jaffe *et al.*, 1971)]. The difficulty in imaging domains arises because of the very small grain size (0.1-0.3 μm) and small tetragonal distortion in many of the lead zirconate titanate films we have examined. Twinning in these fine-grained samples is not always easy to observe. For general imaging purposes, the contrast at the grain boundaries is enhanced if the incident electron beam is tilted by 15°-20° from the specific crystallographic orientation of a selected ferroelectric grain. The contrast is further improved by forming an electron image with the undeflected beam and 2-4 diffracted beams. Most images have been obtained near [100], [110], and [111]

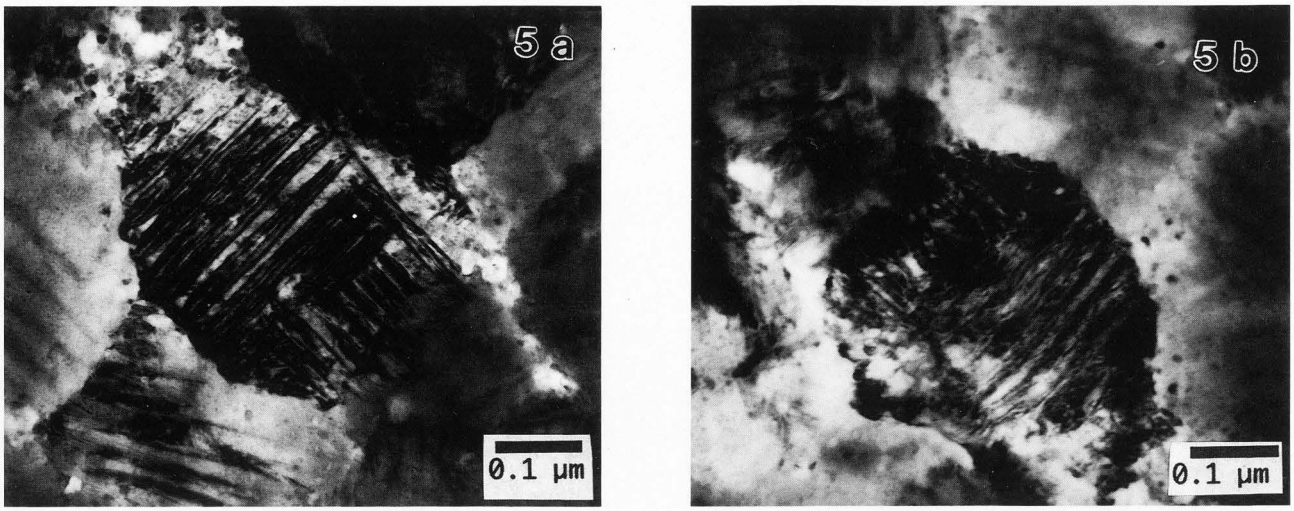

Figure 5. Transmission electron micrographs of a sol-gel deposited, La-doped PZT film with the same composition as the sample in Figure 3. The two micrographs illustrate the domain morphology of these ferroelectric films. (**a**) Virgin sample (no thermal cycling); (**b**) same sample after in-situ heating and cooling in the microscope (RT-300°C-RT).

poles using a cubic perovskite cell (Goral *et al.*, 1990).

Several of the films have also been analyzed by nanoprobe EDS (Huffman *et al.*, 1992a). The general trend in all the rf-sputtered PZT films (doped or undoped) is that the Zr/Ti ratio is close to that of the target material. Since excess Pb is present in the ceramic targets in order to ensure the incorporation of the correct amount of Pb in the films, the Pb content in the films can vary. Films with good electrical properties are very close to stoichiometric. In the sol-gel deposited films, the annealed samples have a composition close to the starting materials. Pb is quite difficult to analyze, and it also interferes with the other elements in these films (Reaney and Barber, 1990; Huffman *et al.*, 1992a). Matrix effects cannot be ignored when analyzing these materials via EDS. Excessive milling results in Pb loss from the films. Furthermore, prolonged exposure under the beam and/or in-situ heating in the TEM also result in driving Pb off the specimens. However, we obtained good general analyses and, by combining them with more bulk techniques [e.g., wavelength dispersive spectroscopy (WDS), secondary ion mass spectrometry (SIMS) and Auger spectroscopy (Bruchhaus *et al.*, 1992; Sudhama *et al.*, 1992), one can keep track of fluctuations in composition, segregation of dopants, or other issues that affect overall device characteristics.

Conclusions

Electron microscopic techniques are very useful tools for characterizing thin-film oxide ceramic materials. We have shown these techniques to provide critical information about thin-film ferroelectric materials that allows them to be integrated in semiconductor devices.

Sample preparation is critical in obtaining the correct information about these ferroelectric films. Ion milling can be used with such parameters so that volatilization of elements such as Pb in these specimens is minimized.

Ultramicrotomy is a promising technique for preparing cross sections of these thin-film structures. There is still a lot of development remaining in order to fully utilize the benefits of this sample preparation method and to document specific sample artifacts.

Ferroelectric thin films are rather sensitive to electron beam interactions and thermal treatments, particularly when they contain lead. Due to their morphology and properties, it is also quite difficult to image ferroelectric/ferroelastic domains in these materials. Lead titanate and titanium-rich films (higher c/a ratio) and samples with larger grain sizes (0.5-1.5 μm) are easier to work with than films having less titanium and very small grain sizes (0.1-0.3 μm).

There can be some compositional variability in these films but on a small scale. Pb is the most difficult element to reliably analyze. More than one analytical technique is necessary to reliably characterize the composition of these materials.

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References

Anderson R, Benedict J (1992) Precision ion milling of layered, multi-element TEM specimens with high specimen preparation spatial resolution. Mat. Res. Soc. Symp. Proc. **254**, 141-148.

Anderson R, Klepeis S, Benedict J, Vandygrift WG, Orndorff M (1989) Recent developments in the preparation of semiconductor device materials for the transmission electron microscope. Inst. Phys. Conf. Ser. No. **100**, 491-500.

Auciello O, Kelly R (1984) Ion Bombardment Modification of Surfaces. Elsevier, Amsterdam.

Bondurant D, Gnadinger F (1989) Ferroelectrics for nonvolatile RAMs. IEEE Spectrum **18**, 30-33.

Bruchhaus R, Pitzer D, Eibl O, Scheithauer U, Hoesler W (1992) Investigation of Pt bottom electrodes for "in-situ" deposited $Pb(Zr,Ti)0_3$ (PZT) thin films. Mat. Res. Soc. Symp. Proc. **243**, 123-128.

Dey SK, Barlingay CK, Lee JJ, Gloerstad TK, Suchital CTA (1991) Advances in processing and properties of perovskite thin films for FRAMs, DRAMs, and decoupling capacitors. Proc. ISIF-91, 3rd Int'l Symp. on Integrated Ferroelectrics, 30-43.

Evans JT, Womack R (1988) An experimental 512-bit nonvolatile memory with ferroelectric storage cell. IEEE J. Solid State Circuits **23**(5), 1171-1175.

Goo EKW, Mishra RK, Thomas G (1980) Electron microscopy study of ferroelectric domains and domain wall structure in $PbZr_{0.52}Ti_{0.48}O_3$. J. Appl. Phys. **52**, 2940-2943.

Goral JP, Huffman M, Al-Jassim MM (1990) TEM investigation of the ferroelectric domain structure in sputtered PZT thin films. Mat. Res. Soc. Symp. Proc. **200**, 225-230.

Huffman M, Goral JP, Al-Jassim MM, Mason AR, Jones KM (1990) Compositional and microstructural characterization of thin film lead zirconate titanate ferroelectrics. Thin Solid Films **193/194**, 1017-1022.

Huffman M, Goral JP, Al-Jassim MM, Echer C (1992a) Structural and chemical composition investigation of thin lead zirconate titanate films. J. Vac. Sci. Technol. A **10**, 1584-1591.

Huffman M, Gealy FD, Kammerdiner L, Zurcher P, Zhu JG, Al-Jassim MM, Echer C (1992b) Microstructural, compositional and electrical characterization of ferroelectric lead zirconate titanate thin films. Ferroelectrics **134**, 303-312.

Huffman M, Schuele PS (1993) Morphology and electrical characterization of calcium modified ferroelectric lead zirconate titanate films. Ferroelectrics **143**, 251-262.

Huffman M, Zhu JG, Al-Jassim MM (1993) Morphology and domain structure of ferroelectric lead titanate and lead zirconate titanate thin films, an overview. Ferroelectrics **140**, 191-201.

Jaffe B, Cook Jr WR, Jaffe H (1971) Non-Metallic Solids, Vol. 3 (Piezoelectric Ceramics). Popper P, Roberts JP (eds.). Academic Press Inc., New York, pp 65-71, 115-134.

Kirk ECG, Williams DA, Ahmed H (1989) Cross-sectional transmission electron microscopy of precisely selected regions from semiconductor devices. Inst. Phys. Conf. Ser. No. **100**, Section 7, 501-506.

Kwok CK, Desu SB (1992) Transmission electron microscopy study of PZT thin films. In: Ceramic Transactions, Ferroelectric Films, Vol. 25. Bhalla AS, Nair KM (eds), pp 73-84 (available from authors).

Lines ME, Glass AM (1977) Principles and Applications of Ferroelectrics and Related Materials. Clarendon Press, Oxford, pp 87-126.

Lucuta PG (1989) Ferroelectric-domain structure in piezoelectric ceramics. J. Am. Ceram. Soc., **72**, 933-937.

Lucuta PG, Teodorescu V, Vasiliu F (1985) SEM, SAED, and TEM investigations of domain structure in PZT ceramics at morphotropic phase boundary. Appl. Phys. A, **37**, 237-242.

Malis TF, Steele D (1990) Ultramicrotomy for materials science. In: Specimen Preparation for TEM of Materials III, Mat. Res. Soc. Symp. Proc. **199**, 3-43.

Malis TF, Steele D (1992) Thickness variations and surface layers in ultramicrotomed sections and their effects on elemental mapping. In: Specimen Preparation for TEM of Materials III, Mat. Res. Soc. Symp. Proc. **254**, 257-270.

Moazzami R, Hu C, Shepherd WH (1990) A ferroelectric DRAM cell for high density NVRAM's. IEEE Electron Device Lett. **11**(10), 454-456.

Popoola OO, Cooper JJ, Jakstys BP, Kriven WM (1992) Application of ultramicrotomy to TEM specimen preparation of particulate inclusion and composite materials. In: Specimen Preparation for TEM of Materials III, Mat. Res. Soc, Symp. Proc. **254**, 271-278.

Randall CA, Barber DA, Whatmore RW (1987) Ferroelectric domain configurations in a modified-PZT ceramic. J. Mater. Sci. **22**, 925-931.

Reaney IM, Barber DJ (1990) Transmission electron microscopy of lead scandium tantalate thin films. J. Microsc. **160**, 213-224.

Roy RA, Etzold KF (1992) Substrate and

temperature effects in lead zirconate titanate films produced by facing targets sputtering. J. Mater. Res. 7(6), 1455-1464.

Sudhama C, Kim J, Chikarmane V, Lee JC, Tasch AF, Myers ER, Novak S (1992) Polarity and area dependence of reliability characteristics of sputtered and sol-gel derived thin PLZT films for DRAM applications. Mat. Res. Soc. Symp. Proc. **243**, 147-152.

Discussion with Reviewers

C.B. Carter: Could the authors elaborate on the observations that lead them to "believe that the pores in the PZT films are created during the annealing."

Authors: We (and others: Kwok and Desu, 1992) have carried out various annealing experiments of rf-sputtered, sol-gel deposited and Ion Cluster Beam deposited lead titanate and lead zirconate titanate films. Depending on the amount of excess Pb in these films, high and prolonged annealing causes a higher concentration of these "micropores" in the films. If the amount of lead in the films is close to stoichiometric, we have seen very good "pore-free" films even after annealing. We also believe that these film features are not simply milling artifacts. Rather, they depend on the composition and processing of the films.

G. van Tendeloo: The authors mention that the small grain size of the PZT films makes it difficult to image domains by the TEM. TEM is supposed to be ideally suited for imaging small features.

Authors: We agree. What we mean, as we made more clear in the text, is that when the grains of the material are 0.2 μm or so, and when the composition of the PZT films is close to the morphotropic phase boundary (MPB), the c/a ratio is very close to one and twinning and domains may be very difficult to see. It is difficult (although we have had some success, Goral *et al.*, 1990) to get a clean diffraction pattern from a single grain to unequivocally observe twinning. Close to the MPB, there is also the question of mixed phases that will also affect the diffraction patterns. For higher Ti content films and lead titanate, it is easy to see twinning and find domains. In the case of bulk ceramic samples, grain sizes are very large (on the order of several micrometers) so that good, single crystal diffraction patterns can be easily obtained and analyzed.