DOI: 10.1017/S1431927605502198
Microsc Microanal 11(Suppl 2), 2005
Copyright 2005 Microscopy Society of America

Passive Layer Formation at Pt/$PbTiO_3$ Interfaces Identified Using STEM and EFTEM

S.J. Welz[1], L.F. Fu[1], R. Erni[1], M. Kurasawa[3], P.C. McIntyre[3], and N.D. Browning[1,2]

[1] Department of Chemical Engineering and Materials Science, University of California Davis, Davis, CA 95616
[2] National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, CA 94720
[3] Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305

Ferroelectric thin film materials are currently under intensive investigation for potential applications in non-volatile random access memories (NVRAMs) due to their unique ferroelectric and dielectric properties [1]. However, degradation issues in ferroelectric materials such as fatigue, imprint and aging limit extensive commercialization in memory and electronic devices [2,3]. Therefore, fundamental studies of non-volatile ferroelectric materials with respect to their structural and electronic properties are mandatory in order to understand the origin of the degradation mechanisms.

This study shows interface reaction at the ferroelectric/electrode interface of a multi layer thin film complex oxide material, which consists of a La_2O_3-doped $SrTiO_3$ substrate, thin films consisting subsequently of $PbTiO_3$ and Pt as well as two lead oxide top layers. Particular attention has been paid on the $PbTiO_3$/Pt interface and the compositional and electronic structure. Analytical techniques include Z-contrast imaging, EELS and EFTEM carried out on a FEI Tecnai F20 UT STEM[4-6].

Fig. 1a shows a low magnification Z-contrast image of the composition of the ferroelectric thin film. The sample is prepared by a unique TEM sample preparation technique combining cleavage and focused ion beam techniques (shadow technique)[7]. The high resolution Z-contrast image in Fig. 1b reveals the epitaxial grown $PbTiO_3$ layer on top of the single crystal $SrTiO_3$ substrate. The $PbTiO_3$ layer as grown should be a single crystal film. However, it is observed near the Pt electrode that the film decomposed forming an intermediate layer. The structure of this intermediate layer is amorphous and its thickness extends to about 10 nm. In addition, nanometer sized precipitates are formed in the decomposed area which agglomerate near the Pt electrode.

EELS analysis has also been performed across the interfaces. The corresponding low-loss and core-loss EEL spectra of the layers are shown in Fig. 2a and 2b. The energy-loss near-edge structure (ELNES) analysis of these spectra indicates the distortion or loss of symmetry in the Ti-O bonds and loss of lead in the amorphous intermediate layer. Quantitative analysis of these spectra shows that this amorphous region is an intermediate Ti-rich phase between TiO_2 and $PbTiO_3$, which is also confirmed by EFTEM. The nano-crystalline precipitate near the Pt electrode is determined to be a Pt- and Pb-rich crystalline phase.

These structural features could be the origin of the inferior reliability of ferroelectric switching typically observed for Pt-electrode ferroelectric capacitors. This is supported by the fact that the $PbTiO_3$ film decomposes and forms a structure-distorted intermediate layer. As a result, it acts as a ferroelectrically dead area or a passive layer which interferes with efficient screening of the ferroelectric polarization. The interface reaction which leads to passive layer formation evidently involves reaction of Pb in the ferroelectric film with the Pt electrode to form the Pb/Pt rich

https://doi.org/10.1017/S1431927605502198 Published online by Cambridge University Press

precipitates in the intermediate layer. This is further indicated by the formation of locally thinned Pt electrode regions (marked by the black arrows in Fig. 1a)[8].

References

[1] M.B. Kelman et al., *Appl. Phys. Lett.* 80 (7)(2002) 1258.
[2] L.F. Schloss et al. *J. Appl. Phys.* 93 (3)(2003) 1743.
[3].A.K.Tagantsev et al., *J. Appl. Phys.* 96 (11)(2004) 6616.
[4] D.A. Muller et al., *Nature* 430 (2004) 657.
[5] N.D. Browning et al., *Micron* 28(5) (1997) 333.
[6] R.F. Klie et al., *Phy. Rev. B* 68 (21)(2003) 214101.
[7] S.J. Welz et al., to be submitted to *Ultramicroscopy* (2005)
[8] This research was supported by the Department of Energy under Contract No. DE-AC03-76SF00098 and funded by NSF 0205949. Dr. T. Mizoguchi is gratefully acknowledged for helpful discussions for EELS analysis.

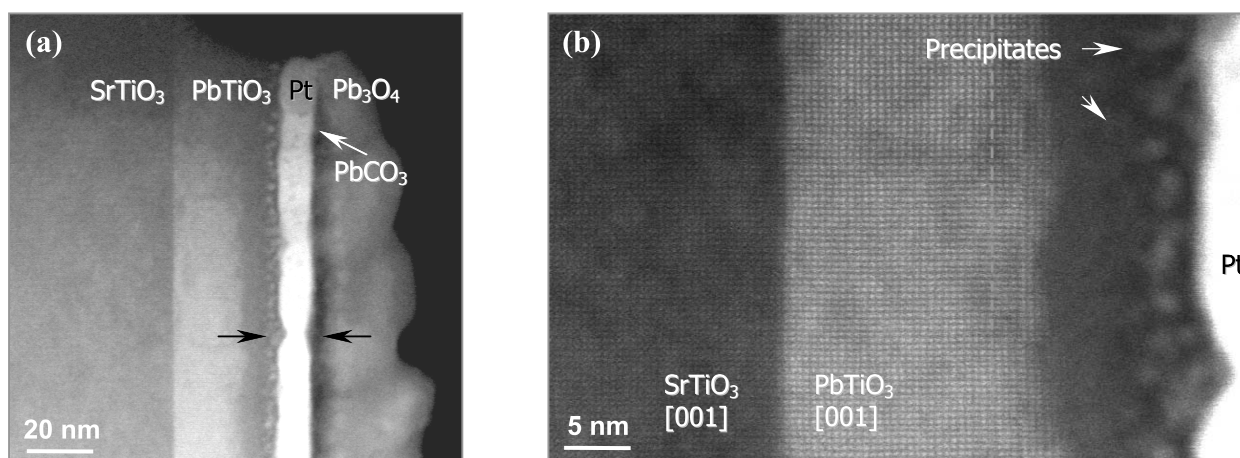

FIG. 1. Low(a) and high(b) resolution Z-contrast images showing the structural composition of the ferroelectric thin films.

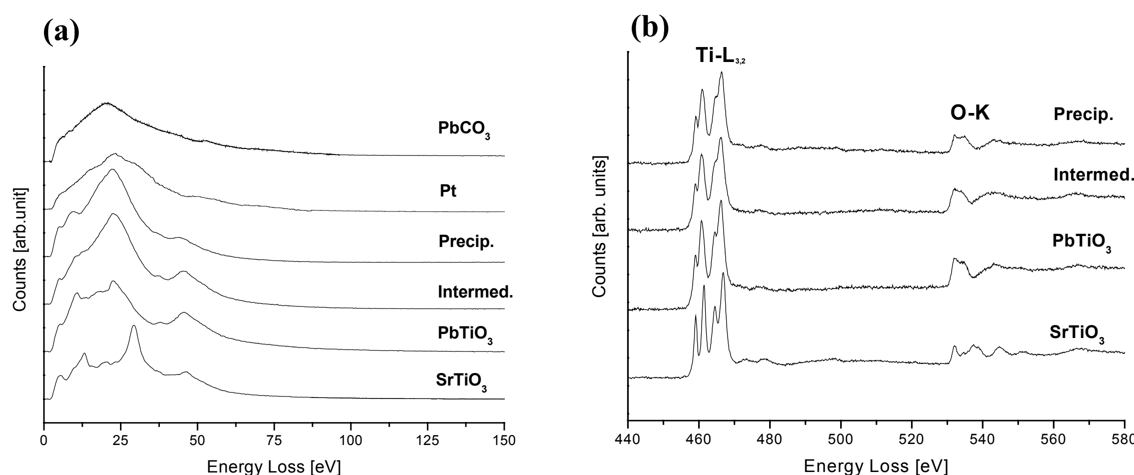

FIG. 2. Low-loss (a) and core-loss (b) EEL spectra from different areas in $PbTiO_3$ thin films.