STOICHIOMETRY AND INTERDIFFUSION IN PZT THIN FILMS STUDIED BY TRANSMISSION ELECTRON MICROSCOPY

L. SAGALOWICZ, P. MURALT, S. HIBOUX, T. MAEDER, K. BROOKS, Z. KIGHELMAN AND N. SETTER
Ceramics Laboratory, Materials Department, EPFL Swiss Federal Institute of Technology, CH-1015-Lausanne.

ABSTRACT

Electrode stability, interdiffusion, phase purity and deviation from stoichiometry at the PZT-electrode interface are key issues in PZT thin film integration. This article highlights the use of transmission electron imaging combined with energy dispersive spectroscopy (EDS) for the investigation of these phenomena. The accuracy of the EDS analysis is discussed. It will be shown that using a standard PZT sample and controlled conditions, reliable analysis can be performed.

Diffusion mechanisms have been studied for Pt based electrode systems and RuO_2-based electrode systems developed for direct integration onto silicon. The materials studied were composed of stacks of silicon-silicon oxide, an adhesion layer (Ti, Ta or TiO_x), an electrode (Pt or RuO_2) and PZT (45/55). The PZT was deposited by sol gel using the same parameters to allow for comparison of the different electrodes. Four different electrode / adhesion layer materials were compared (Pt/Ti, Pt/TiO_x, Pt/Ta and RuO_2 / TiO_2). In the case of Pt, lead and oxygen diffusion through the electrode is observed. While the initial Ta layer transforms into a homogeneous pyrochlore phase, the Ti adhesion layer is heavily deformed. In the case of TiO_x the lead is mainly incorporated at the interfaces with Pt and with SiO_2. No lead diffusion to the adhesion layer is observed for the RuO_2 electrode. In-situ sputtering and sol-gel deposition of PZT are also compared. The sol-gel films are close to the right stoichiometry for the perovskite while the sputtered films contained an excess of lead. No sign of second phase is found by X-ray diffraction (XRD), by EDS and by high resolution transmission electron microscopy (HRTEM) which suggests that the excess lead is accommodated in the perovskite lattice.

INTRODUCTION

$Pb(Zr,Ti)O_3$ (PZT) thin films are used for their ferroelectric, piezoelectric and pyroelectric properties. It is often difficult to control the stoichiometry of the PZT. In addition, to obtain good crystallinity, a final annealing around 650°C is needed. This high temperature is often associated with volatilization of the lead and with interdiffusion between the PZT and the electrodes.[1,2] This may affect the mechanical stability of the device and may result in the presence of defects in the active layer.[3,4]

It is of interest to find methods to characterize the stoichiometry of the PZT and to determine if diffusion between the layers occurs. The easiest methods to determine the stoichiometry of the PZT are Rutherford Back Scattering (RBS) and microprobe analysis. Unfortunately, they just give an average of the composition. EDS analysis of a transmission electron microscope (TEM) sample is local but it is often described as being unreliable since lead evaporation and redeposition may take place during TEM sample preparation and observation.[1] For the active materials, stoichiometry is important since change of stoichiometry may lead to a change in the electrical properties and the appearance of second phases.

Mat. Res. Soc. Symp. Proc. Vol. 596 © 2000 Materials Research Society

It is also of prime interest to know if diffusion between the layers occurs since it can lead to delamination or change in stoichiometry. This may lead to the formation of secondary phases, and consequently, altered properties. The diffusion behavior depends on the electrode materials. For example, a comparison between Pt and IrO_2 electrodes showed that the oxidized electrode IrO_2 is a better diffusion barrier than Pt[5]. RuO_2 was shown to be a good diffusion barrier as well.[6]

The aim of the present study is twofold. Firstly, to describe how reliable EDX measurements can be made. Secondly, to compare different electrodes: Pt/Ti, TiO_2/Pt/TiO_x, TiO_2/Pt/Ta, RuO_2/TiO_2 and TiO_2/RUO_2/TiO_2, and to show how diffusion and stoichiometry can affect the microstrucuture.

RESULTS

Determination of the stoichiometry by EDS

The quantitative determination by EDS of the composition of the PZT is difficult since at low thicknesses lead loss and lead redeposition can occur and at higher thicknesses absorption cannot be neglected. In addition, the Cliff-Lorimer factors (k) used to determine the composition need to be known accurately. Therefore, a standard sample has to be used. The stoichiometry of the standard sample was the following : $Pb_{1.02}Zr_{0.53}Ti_{0.47}Nb_{0.02}$ (within 1% for each element). The parameterless method developed by VanCapellen was also used.[7] This method does not involve a direct determination of the TEM sample thickness. The method consists in plotting the composition as a function of the net counts of a characteristic line of one element. The content in each element was plotted (Fig.1) as a function of the normalized Ti counts for the K-lines (the Ti count is divided by the time of the analysis and the current density of the electron beam). The slope observed on the experimental curves (Fig.1) corresponds mainly to absorption.

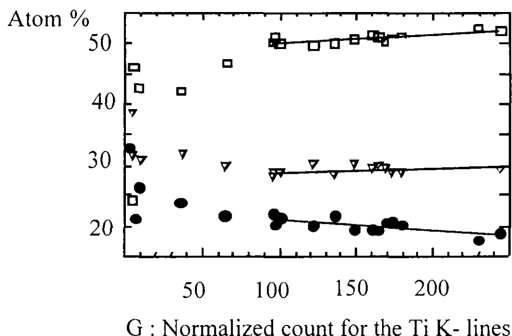

Figure 1 : Atomic content of the PZT. Pb is represented by open squares, the Zr is represented by open triangles and Ti is represented by close circles. Notice that the compositions for G smaller than 90 are very far from the nominal composition but the values for G larger than 90 can be used in a reliable way.

It is observed that the composition, corresponding to net counts of a Ti (representing the thickness) smaller than a given value must be eliminated since large lead losses and lead redepositions have occurred. For large thicknesses, the absorption corrections become important and it is better not to work with those thicknesses. But there is a window of thicknesses for which EDS analysis can be used in a reliable way. The method enables the correction of the Cliff-Lorimer factors (k) used and allows compensation for absorption. More importantly, it

indicates the best thicknesses to work with (in particular where surface effects are negligible). The measurements are done at liquid nitrogen temperature to avoid excess beam heating.

The uncertainty of the method is estimated to be about 2-3% on each absolute content when only the metallic species are considered. It was also checked that the method gave correct results when the PZT compounds take the pyrochlore or fluorite structure. For the high thicknesses used, significant variations in lead content could not be detected during successive EDS measurement indicating that lead loss or redeposition is negligible. The lead content determined by our method was always in agreement (within 2%) with that determined from microprobe or RBS analysis when the sample was homogeneous enough. The uncertainity on the Zr:Ti ratio is more difficult to know since this ratio often varies significantly. The microprobe analysis gives an average composition over a large area and the TEM analysis is very localized. The main limitation of the proposed method is that only thick areas can be used losing some spatial resolution associated with the TEM analysis.

Description of the substrates to be compared

PZT was deposited onto an SiO_2/Si substrate (SiO_2 : 1μm) coated with an adhesion layer (Ti, Ta or TiO_x), the electrode material itself (Pt or RuO_2), and when necessary a seed layer of TiO_2. The electrodes which were compared were : Pt(100 nm) / Ti(10 nm), TiO_2(2 nm) / Pt(100 nm) / Ta(10nm), TiO_2(2nm) / Pt(100nm) / TiO_x(25 nm) and TiO_2(2 nm) / RuO_2(100 nm) / TiO_2(30 nm). The different layers beneath the PZT were deposited at 400°C except the RuO_2 which was deposited at 500°C. A temperature of 400°C for the Pt is the maximum for which a (111) orientation can be obtained. The PZT was prepared by a sol-gel route with a final annealing at 650°C for 15 min.

Features common to all the films

The grain structure of the PZT appears to be columnar with an average width of 100-150nm (Fig.2) which is in full agreement with the plan view images (Fig.3). No evidence of second phase was found within the PZT by SEM and TEM. EDS analysis reveals that the Pb content was always close (within 2 % which corresponds to the uncertainity of the method) to that of the stochiometric perovskite. The contrast present in the dark field images indicates that some structural defects are present. Those are probably low angle grain boundaries, dislocations and domains. This is partly due to the relatively low temperature of the deposition method.

Figure 2 : Dark field cross section TEM image showing the columnar structure of the 45/55 PZT films obtained by sol-gel deposition.

Figure 3 : Dark field plan view image showing the surface of the PZT 45/55 (deposited on RuO_2). No sign of second phase in the grain interior and in the grain boundaries is present. 90° domain walls are clearly visible (arrowed).

Features common to all films deposited onto Pt electrodes

The Pt electrodes in all cases show a columnar structure with an average grain size of 50-100nm. XRD demonstrates that the Pt and the PZT films are (111) oriented. For our deposition conditions, it is found that the Pt electrode is not an efficient barrier to diffusion. In all cases, some Pb and oxygen are detected in the adhesion layer. Defects which have a diameter less than 10 nm are also present at the interface Pt-PZT (not shown here). The defects often lie on Pt grain boundaries, indicating that they are the result of diffusion with the bottom electrode. Sometimes they appear as porosity within the TEM sample. However, since the fluorite contains more defects (porosity, weaker bonds) than the perovskite, it will disappear first in the TEM-sample preparation and the porosity may correspond to the removal of this fluorite phase. Pb diffusion to the bottom electrode would prevent the PZT from having the right stoichiometry close to to the interface and the perovskite will not nucleate in this region. The fluorite, which is more tolerant to changes in composition, would be present instead. It is therefore concluded that both porosity and fluorite may be present at the PZT/Pt interface and are likely to result from diffusion between PZT and Pt.

Differences between films obtained for the Pt electrodes using different adhesion layer

a. Pt (100 nm) / Ti (10 nm) substrate

The Ti adhesion layer looks irregular (fig. 4a) because of diffusion. The adhesion layer seems also very porous and the interfaces with the SiO_2 and Pt are not well defined. Precipitates rich in Pt were also found in the adhesion layer, and it was also determined that an important amount of Pb is present in the Ti (%Pb/(%Pb+%Ti) $\approx$ 0.15) and in the SiO_2 close to the adhesion layer. XPS shows that the adhesion layer is oxidized.

b. Pt (100 nm) / Ta (10 nm) substrate

The adhesion layer and the Pt appear more regular than in the case of the Ti (Fig.4b). It also appears thicker (40 nm instead of about 30 nm) than in the case of the Ti. A large amount of Pb is present in the adhesion layer but it is uniformly distributed (%Pb/(%Pb+%Ta)) $\approx$ 0.3. The diffusion of Pb and oxygen corresponds to the stabilization of a TaPbO phase. Peaks corresponding to this compound were found by XRD.

c. Pt (100 nm) / TiO_x (25 nm) substrate

In the case of TiO_x adhesion layer, little deformation (Fig.4c) is observed and the TiO_x layer is not too much affected by diffusion of other metallic species. However in the Pt-TiO_x interfaces and in the SiO_2/TiO_x interfaces, defects are present. EDX analysis reveals that the content of lead is maximum in the SiO_2 close to the adhesion layer. An intermediate layer is also present between TiO_x and Pt. It contains some lead and probably Ti and Pt. In the middle of the adhesion layer the Pb content is relatively low : (%Pb/(%Pb+%Ti)) $\approx$ .04. This is the adhesion layer for which the lowest amount of lead diffusion is detected and the observed diffusion may be associated with the fact that the titanium is not completely oxidized since the adhesion on fully oxidized Ti is insufficient and Pt orientation is affected as well. The adhesion layer TiO_x is a trade off between adhesion and Pt orientation on one hand (Ti is the best) and chemical stability on the other hand (TiO_2 is probably the best).

d. Deposition onto TiO_2 (2 nm) / RuO_2 (100 nm) / TiO_2 (25 nm)

The RuO_2 is also columnar with a grain width of 40nm (not shown here). The interface between RuO_2 and PZT is very rough. The TiO_2 adhesion layer appears unaffected by the deposition of PZT (Fig.4d) and no Pb was found in this adhesion layer. The RuO_2 appears therefore to be a much better diffusion barrier than Pt.

Deposition by in-situ sputtering at 570°C (compared to sol-gel deposition)

The diffusion behavior between the PZT and the electrode was very similar to what is observed for the sol-gel deposition. However a difference concerns the stoichiometry of the PZT. In sputtering, an excess lead was also used to compensate for Pb evaporation. EDS and Rutherford back scattering (RBS) analysis demonstrate that the films, which did not show any second phase by XRD, were also rich in lead. This is different from the films deposited by sol-gel which were close to the perovskite stoichiometry. A film for which the atomic ratio Pb/(Zr+Ti) was 58/42 was analyzed by plan view and cross-section TEM. The content of Pb was very homogeneous. In particular, EDS indicates that there was no excess lead in, or close to, the grain boundaries. No sign of second phase (in the grain interior and in the grain boundary) could be found by XRD and HRTEM (Fig.5). This suggests that the excess lead is incorporated within the perovskite lattice in the B site as proposed for the case of the perovskite $Pb(Sc_{1/2}Ta_{1/2})O_3$ which was also obtained by in-situ sputtering.[8]

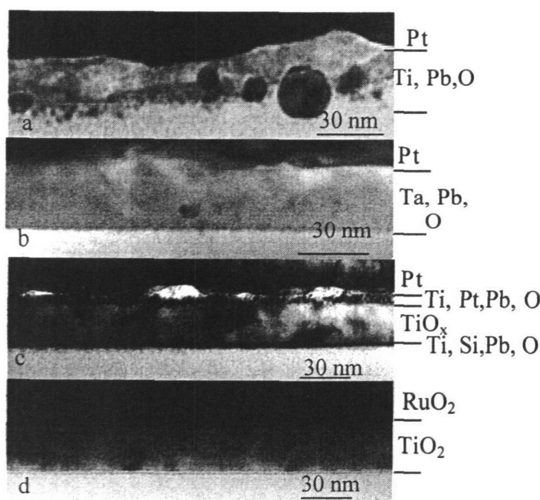

Figure 4 : Bright field images of different adhesion layer-electrode materials. (a) Pt/Ti : lead and oxygen diffusion is obseved in the Ti (b)Pt/Ta: lead and oxygen diffusion in the Ta is observed. (c) Pt/TiO_x: lead diffusion is observed at the Pt/TiO_x and at the SiO_2-TiO_x interface is observed. (d) RuO_2/TiO_2: no lead diffusion is observed.

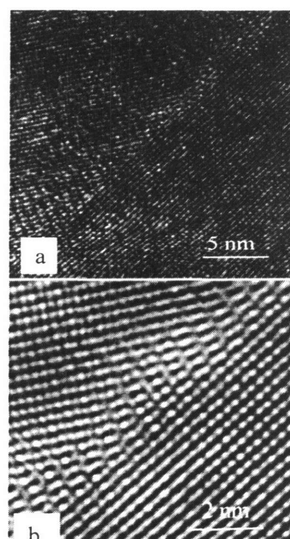

Figure 5 : HRTEM images of PZT in a sample containing an excess of lead. (a) normal image, (b) enlarged and filtered image of (a). There is no sign of second phase. The grain at the bottom is [110] oriented and the grain at the top is [211] oriented.

DISCUSSION

We discuss here the mechanisms of diffusion. It is first observed that oxidized electrodes and adhesion layer are more stable than the non-oxidized ones. It is therefore believed that the oxidation and reaction with the adhesion layer are important driving forces for diffusion. The cases of Ti and Ta appear different. In the case of Ti, a lot of deformation and diffusion (Pt, Pb, Si) are observed. In the case of Ta, the layer is thicker and much more regular. The difference in behavior might be understood when one knows that in the oxide Ti diffuses more than oxygen while Ta diffuses slower than oxygen.[9] In a previous study,[9] we showed that when one oxidizes the electrode (without depositing the PZT), almost all the Ti comes to the Pt surface while most of the tantalum stays under the Pt. In the case of Ti, there is upward diffusion of Ti, which leaves a lot of vacancies and voids, which are at least partially filled by downward diffusion of oxygen, lead and Pt. In the case of Ta, there is little diffusion of Ta through the platinum electrode but lead and oxygen diffuse down to stabilize a PbTaO phase, which forms a regular layer. The TiO_x adhesion layer is also different since it is already oxidized and relatively stable. In that case, during PZT deposition, diffused species are mainly present at the interfaces with Pt and SiO_2 and in the SiO_2 where it may form a lead silicate oxide.

The Ti adhesion layer is probably the worst since it is very irregular and a lot of diffusion is observed. Ta is probably relatively good concerning the mechanical stability. The observed layer is homogeneous and not much deformation of the platinum is present. However, it still corresponds to a high quantity of lead diffusion, which may correspond to presence of defects at the Pt-PZT interface. With the TiO_x adhesion layer there is less diffusion but when this diffusion occurs, it is found at the interfaces, which may affect the mechanical stability of the device.

ACKNOWLEDGMENTS

This research was founded by the Swiss priority program on materials research and by the Swiss priority program on optics. The electron microscope work was performed at the CIME (EPFL). Finally we would like to thanks L. Gerard and D. Laub for help with the TEM sample preparation, and Dr. D. V. Taylor and Dr. A. Seifert for helpful discussions.

REFERENCES

1. I. M. Reaney, K. Brooks, R. Klissurka, C. Pawlaczyk, and N. Setter, J. American Ceram. Soc. **77,** 1209-1216 (1994).
2. P. D. Hren, S. H. Rou, H. N. Al-Shareef, M. S. Ameen, O. Auciello, and A. I. Kingon, Integrated Ferroelectrics **2,** 311-325 (1992).
3. C. Voisard, K. B. Brooks, I. M. Reaney, L. Sagalowicz, A. L. Kholkin, N. Xanthopoulos, and N. Setter, J. European Ceramic Society **17,** 359-367 (1997).
4. S. G. Gap, K.-T. Shim, and Y.-H. Lee, Jpn. J. Appl. Phys. I **38,** 217-218 (1999).
5. T. Nakamura, Y. Nakao, A. Kamisawa, and H. Takasu, Jpn. J. Appl. Phys. **33,** 5207-5210 (1994).
6. T. Maeder, P. Muralt, L. Sagalowicz, and N. Setter, Journal of the Electrochemical Society **146,** 3393-3397 (1999).
7. E. Van Cappellen, Microsc. Microanal. Microstruct. **1,** 1-22 (1990).
8. R. W. Whatmore, Z. Huang, and M. Todd, J. Appl. Phys. **82,** 5686-5694 (1997).
9. T. Maeder, L. Sagalowicz, and P. Muralt, Jpn. J. Appl. Phys. **37,** 2007-2012 (1998).