

Lead enrichment at the surface of lead zirconate titanate thin films

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Abstract

Ferroelectric thin films have been investigated intensely by many researchers over the past decade, but some important phenomena that influence the electrical properties have been overlooked. This work addresses the lead enrichment, which is observed on the surface of lead zirconate titanate films.

The XPS compositional profiles of PZT films prepared using different thermal treatments are presented and correlated with the preparation conditions.

The segregation profiles are explained in terms of a simple oxidation model that induces the diffusion of lead to the surface. The ionic diffusion also induces self-polarisation, commonly seen in ferroelectric films. The implications on the electrical properties of ferroelectric films, particularly, imprint of the polarisation state, are also discussed.

Introduction

Ferroelectric thin films have been studied intensely over the last 15 years, however, an aspect of their solid state chemistry, notably the enrichment of various at the top surface [Watts et al., 2001, #44257][Impey et al., 1998, #2423] exposed to the ambient during heat treatment, has been overlooked. This is surprising since defects, chemical homogeneity and phase separation are important to the properties of the films.

Lead enrichment is commonly observed at the top surface of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) films which seems to contradict claims that evaporation causes Pb depletion after high temperature

annealing.

The results of X-ray photoelectron spectroscopy (XPS) performed on $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3)$ thin films are reported. Compositional profiles have been determined along with an analysis of the state of oxidation of the lead. The data are compared with bulk polycrystalline material as standard. A model is described briefly that accounts for the diffusion and surface enrichment in the films.

Experimental Method

The films were deposited on platinised silicon substrates ($\text{Si}/\text{SiO}_2/\text{TiN}/\text{Pt}$) by sol gel methods using a synthesis and described in detail previously [Chiorboli et al., 1997, #22138] [Watts et al., 2002, #19410]. A combined pyrolysis and crystallisation at 600 °C in a tube furnace was used for each of the 5 layers deposited.

Bulk, polycrystalline PZT was used as a comparative sample to standardise the XPS results. These were prepared using normal ceramic methods including, ball milling calcination pressing and sintering under an overpressure of Pb.

An Escalab MkII (VG Scientific), equipped with a 5-channeltron detection system and a standard Al K α excitation source ($h\nu = 1486.6$ eV), was employed for the XPS experiments. Selected-area XPS depth profiles were acquired by using 1.0 and 2.0 keV energy Ar^+ beam, rastered over an area of the window in the Au mask. In selected-area mode, the photoelectrons were collected from the sample area of diameter 1 mm. More experimental details on XPS depth profiling have been published elsewhere [Kaciulis and Mattogno, 2000, #21490].

X-ray powder diffraction patterns were recorded with a Philips PW 1050r25 modified diffractometer, using CuK_α radiation to confirm the presence of perovskite PZT.

Results and Discussion

The X ray diffraction analyses shower the crystallisation of the prevalent perovskite phase in the films deposited. The film was well oriented having an intense (111) peak.

The concentration profile a PZT film sample is shown in Figure 1. The film has been etched

and analysed progressively down to the Pt electrode. The histograms presented in Figure 2 are the relative concentrations of Pb, Zr and Ti determined by XPS. It shows that the surface concentration is higher, but, after removing the top layer by sputtering or lapping, the values are close to the nominal composition. Hence, there is some surface segregation on the bulk sample but it is not as high as on the film. Surface segregation of Pb has been attributed to preferential sputtering. In these experiments sputtering was carried out using energies of 1 and 2 keV. The higher energy (2 keV) did result in a higher lead value at the film surface but the increase was still present even using lower energies. Thus, the surface segregation is present in thin films and is of a higher magnitude than on the surface of bulk ceramics.

Figure 3 shows the Pb 4f spectrum, determined using XPS, of a PZT film after 80 minutes sputtering. The fitted Pb⁰ peak is of similar magnitude to the Pb²⁺ peak. This might suggest that there is a considerable amount of reduced lead in this sample but such spectra should be carefully interpreted as metals can be reduced as a consequence of the sputtering. Figure 4 shows how the Pb 4f spectrum in the bulk sample changes with sputtering time. Clearly, the lead is reduced but even after 240 minutes sputtering the shoulder due to the Pb⁰ peak is lower than in Figure 3. Therefore, it is quite likely that reduced lead is present in the film.

Although surface enrichment of some elements has been reported by many authors [Gusmano et al., 2002, #21636] [Watts et al., 2001, #44257] [Impey et al., 1998, #2423] there are few explanations for this phenomenon. An analogy may be drawn with the oxidation of metals such as Cu and Sn where the metals diffuse towards the reacting surface. This has been described by Wagner [Wagner, 1933, #44734] and by Cabrera and Mott [Cabrera and Mott, 1948, #37343]. The data presented here indicates that the pyrolysis and crystallisation steps result in incomplete oxidation. In fact, sol gel methods are notorious for the reducing conditions that are present during pyrolysis [Gusmano et al., 2002, #21636] [Polli and Lange, 1995, #4643]. In this case, the diffusion is driven by the oxidation of Pb at the PZT/oxygen interface. A second mechanism that could explain this type of segregation is kinetic demixing [Martin, 2003, #16279]. If an oxygen concentration gradient exists then the metallic species will diffuse at different rates, usually in the direction of higher oxygen potential even though the phase is thermodynamically stable. Kinetic demixing is often treated for solid solutions

but it has been shown that a single phase can decompose under a chemical potential gradient. [Wang and Akbar, 1992, #22305]. It is difficult to separate the contributions of the thermodynamically driven diffusion or kinetic demixing as the low oxygen content in the film promotes both processes. Indeed, it is likely that both are taking place.

The consequences of surface segregation have been discussed [Watts et al., 2004, #38258]. As illustrated in Figure 5, the migration of cations in the film at high temperatures sets up an electrical potential that polarises the ferroelectric as it cools through the Curie temperature. This in turn allows the cations to diffuse faster and is a reason why surface enrichment is so marked in ferroelectric films. The self-induced polarisation is in the direction observed, experimentally, by Impey et al. [Impey et al., 1998, #2423] and by Okamura et al., who noted that self poling near the Curie point leads to imprint or non reversible polarisation [Okamura et al., 1999, #39115].

Conclusions

X ray photoelectron spectroscopy shows lead segregation at the surface of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin films, prepared by sol gel methods. Evidence for oxygen deficiency has been found although the reduction of Pb^{2+} to Pb^0 because of the preferential sputtering of oxygen is high. These experimental results suggest that the diffusion of lead to the surface in PZT films is a result of either an oxidation of the Pb or kinetic demixing. Both of which would be favoured by incomplete oxidation of the film that increases the oxygen compositional gradient near the film surface.

Hypotheses advanced for surface segregation imply the presence of an oxygen compositional gradient and the fastest moving species (Pb^{2+}) diffuses towards it. This may be the result of an oxidation or kinetic demixing.

Acknowledgements

The authors (BW and FL) would like to thank the European Research Project POLCER and COST Action 528 for financial assistance.

Figure Captions

Figure 1 Compositional profile for PZT thin film determined by XPS

Figure 2. Composition of a bulk ceramic determined by XPS: before sputtering; after lapping the surface; after different sputtering times, using an energy of 2 keV.

Figure 3 Peak fitting for the Pb 4f spectrum, recorded after sputtering for 80 min at 1.0 keV performed on a PZT film.

Figure 4 XPS spectra showing the change of the Pb 4f peaks after different sputtering times.

Figure 5 Self poling mechanism in ferroelectric thin films.

References