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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.

Keywords: Ferroelectric properties; Diffusion; PZT; Spectroscopy; Films

1. 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[1,2] 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 $Pb(Zr,Ti)O_3$ (PZT) films which seems to contradict claims that evaporation causes Pb depletion after high temperature annealing.

In this work the results of X-ray photoelectron spectroscopy (XPS) performed on $Pb(Zr_{0.52}Ti_{0.48}O_3$ 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.

2. Experimental method

The films were deposited on platinised silicon substrates ($Si/SiO_2/TiN/Pt$) by sol–gel methods using a synthesis and described in detail previously.[3,4] A combined pyrolysis and crystallisation at 600 °C in a tube furnace was used for each of the five layers deposited.

Bulk, polycrystalline PZT was used as a reference 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 Ka excitation source (hn = 1486.6 eV), was employed for the XPS experiments. Selected-area XPS depth profiles were

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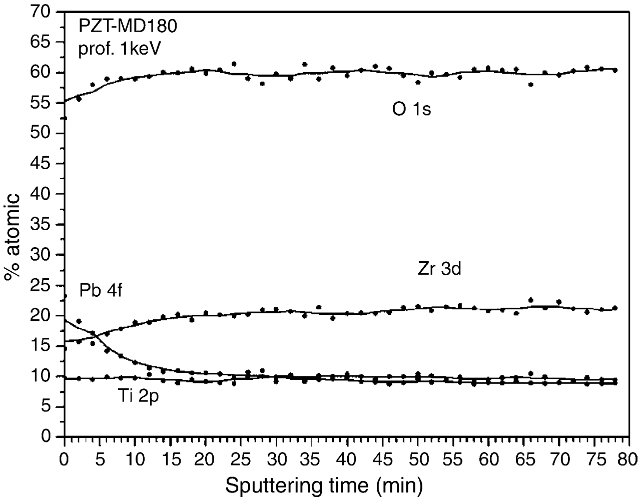

Fig. 1. Compositional profile for PZT thin film determined by XPS.

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.[5]

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

3. 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 (1 1 1) peak.

The concentration profile of the PZT film is shown in Fig. 1. The film has been etched and analysed progressively down to the Pt electrode. The histograms presented in Fig. 2 are relative concentrations of Pb, Zr and Ti determined by XPS for the bulk sample. It shows that the surface concentration of Pb is higher, but, after removing the top layer by sputtering or lapping, the atomic ratios approach the nominal composition. Hence, there is some surface segregation on the bulk sample but it is not as high as on the film. An apparent surface enrichment in Pb could be also caused by preferential sputtering. Depth profiling of the same sample was carried out using ion energies of 1 and 2 keV to check this. Both profiles start from the same lead concentration on the surface, but the higher energy (2 keV) did result only in a slightly lower lead amount in the film volume (after 30 min of sputtering time). This small difference between the profiles, obtained at different energies, allows one to affirm that the surface segregation is really present in thin films and is of a higher magnitude than on the surface of bulk ceramics. An attempt was made to reproduce the work of Impey et al.[2] but the periodic fluctuations were not seen. The conditions needed to produce these variations are particular and in our case the intermediate segregation was probably removed by subsequent thermal treatments.

Fig. 3 shows the Pb 4f spectrum, determined using XPS, of a PZT film after 80 min sputttering. The fitted Pb^0 peak is of similar magnitude to the Pb^{2+} peak. This might suggest that there is a considerable amount of reduced lead in this sample but such spectra should be carefully interpreted as some metals can be reduced as a consequence of the sputtering. Fig. 4 shows how the Pb 4f spectrum in the bulk sample changes with sputtering time. Clearly, the lead is reduced but even after 240 min of sputtering the first peak due to the Pb^0 species is lower than in Fig. 3. Therefore, it is quite likely that some amount of metallic lead is present in the film.

Although surface enrichment of some elements has been reported by many authors[1,2,6] 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 dif-

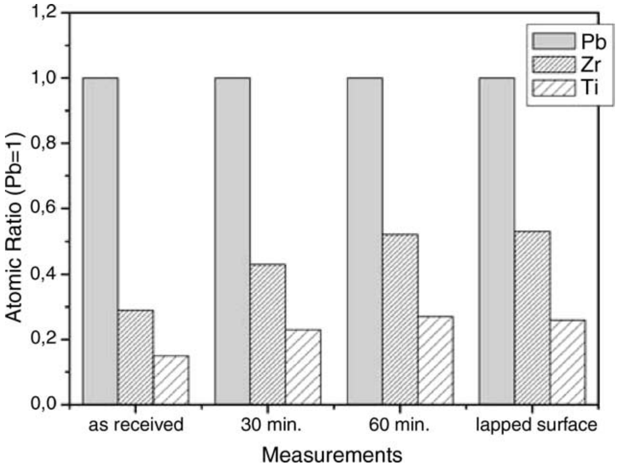

Fig. 2. Composition of a bulk ceramic determined by XPS: before sputtering; after lapping the surface; after different sputtering times, using an energy of 2 keV.

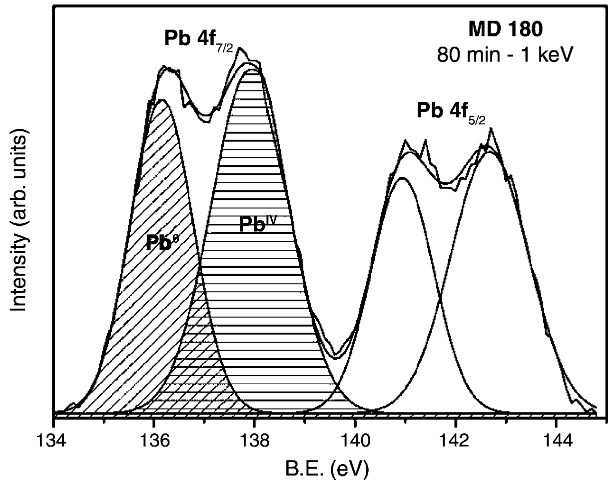

Fig. 3. Peak fitting of the Pb 4f spectrum, recorded after sputtering for 80 min at 1.0 keV performed on a PZT film.

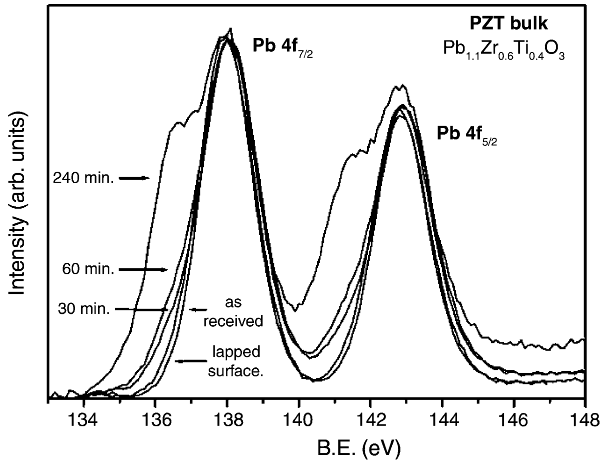

Fig. 4. Comparison of Pb 4f spectra of a bulk ceramic after different sputtering times.

fuse towards the reacting surface. This has been described by Wagner[7] and by Cabrera and Mott[8]. 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.[6,9] In this case, the diffusion is driven by the oxidation of Pb at the PZT/oxygen interface. A second, closely related mechanism that could explain this type of segregation is kinetic demixing.[10] 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 under all these oxygen pressures. Kinetic demixing is often treated for solid solutions but it has been shown that a single phase can decompose under a chemical potential gradient.[11]

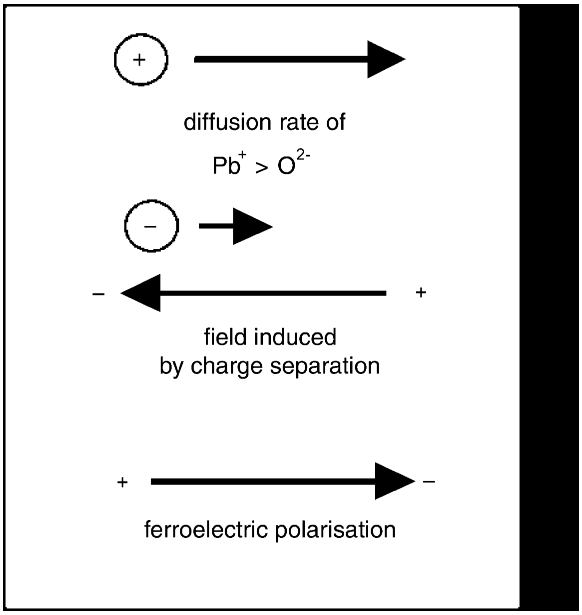

Fig. 5. Self-poling mechanism in ferroelectric thin films.

It is difficult to separate the contributions of the thermodynamically driven diffusion o 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 previously.[12] As illustrated in Fig. 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. The spontaneous polarisation in turn allows the cations to diffuse faster and is the reason why surface enrichment is so marked in ferroelectric films. The ferroelectric polarisation induced electrochemically by this mechanism is in the direction observed experimentally by Impey et al.[2] and by Okamura et al.[13]

4. Conclusions

XPS depth profiling shows lead segregation at the surface of $PbZr_{0.52}Ti_{0.48}O_3$ thin films, prepared by sol–gel methods. Evidence for oxygen deficiency has been found although the reduction of Pb^{2+} to Pb^0 caused by of the preferential sputtering of oxygen is also high.

These experiments suggest that the diffusion of lead to the surface in PZT films is a result of oxidation of the Pb or kinetic demixing, both of which would be favoured by incomplete oxidation of the film during deposition.

Hypotheses are proposed for surface segregation mechanisms that imply the presence of an oxygen potential gradient. (The diffusion of Pb^{2+} may also lead to self-polarisation and imprint.)

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