Interfacial mechanisms controlling phase formation in sol-gel derived lead zirconate titanate thin films

S B MAJUMDER*, V N KULKARNI[†], Y N MOHAPATRA*[†] and D C AGRAWAL*

*Materials Science Programme, [†]Department of Physics, Indian Institute of Technology, Kanpur 208 106, India

Abstract. An RBS study has been carried out to study the relative extent of Pb diffusion in the substrate from PZT films. It is found that extensive diffusion of Pb occurs into the quartz substrate making the film severely deficient in Pb. No such diffusion occurs in the case of PZT films on sapphire and the concentration of Pb is near stoichiometric, except for a small loss due to volatilization. Excessive Pb deficiency, rather than any epitaxial effect, has earlier been proposed by us to be the crucial factor responsible for the existence of the pyrochlore phase in PZT thin films on substrates such as Si, glass, quartz etc. The present results confirm this. The effects of other process variables such as thickness and chemical composition (Zr/Ti ratio) of the film can also be understood in terms of the same phenomenon.

Keywords. PZT; phase formation; sol-gel; thin film.

1. Introduction

Ferroelectric materials display a variety of phenomena which include ferroelectricity (spontaneous electric polarization which can be reversed by an electric field), pyroelectricity (change in electric polarization due to a change in temperature), piezoelectricity (generation of electric charge by application of mechanical pressure or, conversely, production of mechanical strain by application of electric field), high dielectric constant and electro-optic behaviour. This makes these materials useful in a variety of applications (table 1). In the bulk form barium titanate (BaTiO_3) and lead zirconate titanate (PZT) have long been used as capacitors and piezoelectric elements respectively. In the thin film form also they have numerous present and potential applications. Some of these are shown for PZT in table 2. Thin films of lead zirconate titanate (PZT), chemically represented by $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, are currently being studied with increasing interest because of their potential use in piezoelectric, pyroelectric, electro-optic devices and non-volatile memory applications. Phase diagram for PZT is represented as a binary system between lead zirconate (PZ) and lead titanate (PT) (figure 1). In this system a morphotropic phase boundary (MPB) exists between the tetragonal and rhombohedral phases at $x = 0.535$. The compositions near the MPB are of great technological importance because of pronounced maxima in certain properties.

For all applications of PZT, it is desirable to have the material in the ferroelectric perovskite phase, which is readily obtained in bulk and powder form. The as deposited films are usually amorphous and need to be annealed at 500–700°C to form the perovskite phase. However a pyrochlore phase which is cubic and is not

Table 1. Ferroelectric materials—phenomena and applications.

Phenomena	Applications
Dielectric	Capacitors, sensor, phase shifter
Ferroelectric	Non volatile memory
Pyroelectric	Pyrodetector
Piezoelectric	Acoustic transducer, sensor, SAW device, actuator
Electro-optic	Wave guide, optical memory, display modulator

Table 2. Thin film ferroelectric materials and application.

Material	Phenomena	Applications
Pb(Zr, Ti)O ₃ (PZT)	Dielectric	Non volatile memory
	Pyroelectric	Pyrodetector
	Piezoelectric	SAW substrate
	Electro-optic	Wave guide device
(Pb, La) (Zr, Ti)O ₃ (PLZT)	Pyroelectric	Pyrodetector
	Electro-optic	Wave guide device optical memory, SHG display

ferroelectric, first forms at low temperatures (400–550°C) and often does not transform to the perovskite phase at higher temperatures. Thus the film after heat treatment has either the pyrochlore or the perovskite structure. Table 3 summarizes the data from literature. It is seen that factors such as nature of the substrate, thickness of the film, heat treatment conditions etc all influence the phase of the film. In a systematic work carried in our laboratory (Majumder *et al* 1994), films on sapphire, alumina, NaCl and Pt formed a perovskite phase while on quartz, glass and Si the pyrochlore phase was obtained. It was also found that the perovskite structure formed more easily if the film thickness was increased, or if Zr/Ti ratio was decreased or if excess Pb was present.

The initial formation of the pyrochlore phase in thin PZT film has been attributed by us to the presence of a tensile stress in the film in the early stages of heat treatment (Majumder *et al* 1994). The strain energy considerations favour the formation of the pyrochlore phase which is 6.62% less dense than the perovskite phase. The subsequent pyrochlore to perovskite transformation depends as mentioned earlier on various factors which include thickness of the film, nature of substrates, composition, temperature etc. A crucial factor favouring the stabilization of the pyrochlore structure is a deficiency of Pb in the film (Tuttle *et al* 1990; Carim 1991; Krupanidhi *et al* 1992). This is because in the defect pyrochlore structure, represented by A₂B₂O_{7-x}, the BO₆ octahedra are linked together and provide stability to the structure while –A–O chains penetrate the BO₆ octahedra but do not contribute much to the rigidity of the structure (Subramanian *et al* 1983). The pyrochlore thus can tolerate a large deficiency of A (Pb) and oxygen.

A loss of Pb usually occurs during the sintering of Pb based ceramics due to a high volatility of PbO at the sintering temperature (1250°C) (Buckner and Wilcox 1972; Lucata *et al* 1985). In the case of thin films, Pb can additionally be lost

Figure 1. Phase diagram of lead zirconate-lead titanate solid solution.

Table 3. Summary of literature data on phases in PZT film.

Composition	Treatment	Thickness	Substrate	Phase	Ref.
Pb(Zr _{0.5} Ti _{0.5})O ₃	600°C/1/hr	0.1 µm	7059 glass	Pyro	Takahashi <i>et al</i> (1992)
		0.4 µm	7059 glass	Pero	
		0.1 µm	Pt, Al ₂ O ₃	Pero	
		0.4 µm	Pt, Al ₂ O ₃	Pero	
PZT	15 mins at	0.17 µm	sapphire		Kwok <i>et al</i> (1992)
	(i) 450°C			Amorphous	
	(ii) 550°C			Pyro	
	(iii) 600°C			Pyro + pero	
	(iv) 650°C			Pero	
PLZT	(i) 600°C/30 min	0.5 µm	Au, Pt, Al ₂ O ₃	Pero	Seth and Schulze (1990)
	(ii) 800°C/30 min	0.1 µm	Fused SiO ₂	No crystln	
	(iii) 800°C/30 min	0.1 µm	Si (100) and Si (111)	No crystln	

due to its diffusion into the substrate (Liples *et al* 1986; Seth and Schulze 1990). Such diffusion is likely to be greater in amorphous substrates as compared to inert crystalline substrate. It has been proposed (Majumder *et al* 1994) that the deficiency of Pb caused by such diffusion may in fact be responsible for the retention of the pyrochlore phase rather than any 'epitaxial' effect proposed in some reports (Takahashi *et al* 1990; Krupanidhi *et al* 1992).

To test this idea we have used Rutherford back scattering (RBS) in conjunction with X-ray diffraction (XRD) to investigate interfacial phenomena controlling phase formation in thin films of PZT of morphotropic composition on two typical substrates-fused quartz and sapphire. In this paper we present experimental evidence regarding the role of diffusion at the interface.

2. Experimental

Thin films of approximately same thicknesses (70 to 390 nm) were deposited on amorphous quartz and (1120) sapphire by a sol-gel technique described elsewhere (Majumder *et al* 1994). The composition of the sol was taken to be near the MPB region but with 5 mole% excess PbO i.e. $\text{Pb}_{1.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$. The sol was prepared using lead acetate, zirconium-*n*-propoxide, titanium-4-butoxide, isopropanol, water and ethylene glycol (to avoid cracking of the film). The relative amounts of various chemicals used in a typical sol are given in table 4. The film was deposited by spin coating at 8000 rpm. The coated substrate was dried at 80°C for 20 min. It was then heated at 5°C/min to 400°C and held at that temperature for 30 min to drive off the organics. The temperature was then raised to 600°C and maintained for 6 h followed by furnace cooling. The thickness of the film was measured by a surface profilometer (Alpha Step-100, Tencor Instruments USA) and phases of the films were evaluated by X-ray diffractometer (Rich-Seifert Iso-Debyeflex 2002, Germany) using Cu K α radiation with a monochromator. RBS spectra were obtained using 1.7 MeV He⁺ ions from 2 MeV Van-de-Graff accelerator facility. The back scattered particles were detected using a silicon surface barrier detector kept at a backscattering angle of 150°. All RBS spectra were analyzed using the versatile RUMP software package (Doolittle 1985, 1986).

3. Results and discussion

Figure 2 shows the X-ray diffractograms for films of different thicknesses (a) on sapphire and (b) on fused quartz substrates. All the films on sapphire are in perovskite phase irrespective of thickness. We have checked it down to 450 Å on sapphire substrate. On the other hand the first two relatively thinner films on quartz (IIA and IIB) do not show any peak whereas sample IIC which is 3900 Å thick yields a pyrochlore phase. We have also observed, in agreement with earlier reports, that films thicker than 1.5 µm on quartz yield a perovskite phase. Note that the failure to obtain XRD peaks in samples IIA and IIB cannot be due to decreased volume of the material as seen by X-ray since on sapphire the sample as thin as 450 Å yields peaks corresponding to the perovskite phase under similar conditions.

Figure 3a shows RBS spectra—both experimental (dotted) and simulated (solid line)—for the films on sapphire substrate. The structures used for simulation are given in table 5. Simulated compositions of the film agree with nominal composition

Table 4. Typical composition of the coating sol used in the present study.

Material	Moles
Lead acetate	1.05
Acetic acid	6.60
Zirconium- <i>n</i> -propoxide	0.53
Titanium-4-butoxide	0.47
Water	0.52
Ethylene glycol	0.44

Figure 2. X-ray diffractograms of films on I : sapphire (11 $\bar{2}$ 0) and II : quartz, the perovskite phase is obtained on sapphire and the pyrochlore phase on quartz.

except for a small difference in Pb concentration. The thicknesses of simulated layers are also in agreement with profilometer measurements.

Figure 3b shows RBS spectra of the films on quartz substrate. In contrast with sapphire substrate, where the RBS spectra could be perfectly simulated using only one layer, it was found necessary to invoke multilayer structures of differing

compositions to obtain simulated RBS spectra shown by solid lines in figure 3b (i–iii). These structures are listed in table 6.

For thinner films the high energy peaks corresponding to Pb, Zr and Ti are well separated and absolute concentrations of these heavy elements can easily be

Figure 3a. For caption, see p. 1011.

Figure 3. a–b. a. RBS spectra of PZT films of different thicknesses on sapphire (i) 70 nm, (ii) 155 nm, (iii) 280 nm; the arrows indicate the surface positions of the element shown and b. RBS spectra of PZT films of different thicknesses on fused quartz (i) 70 nm, (ii) 140 nm, (iii) 390 nm; the arrows indicate the surface positions of the element shown.

Table 5. Summary of X-ray and RBS results for PZT films on sapphire (11 $\bar{2}$ 0).

Sample no.	Film thickness (nm)	X-ray phase	RBS simulation structure	Layer thickness (Å)	Layer #
IA	70	Perovskite	Pb _{0.92} Zr _{0.53} Ti _{0.47} O ₃	700	1
			Al ₂ O ₃	15000	2
IB	155	Perovskite	Pb _{0.92} Zr _{0.53} Ti _{0.47} O ₃	1550	1
			Al ₂ O ₃	20000	2
IC	280	Perovskite	Pb _{1.0} Zr _{0.53} Ti _{0.47} O ₃	3000	1
			Al ₂ O ₃	20000	2

Table 6. Summary of X-ray and RBS results for PZT films on fused quartz.

Sample no.	Film thickness (nm)	X-ray phase	RBS simulation structure	Layer thickness (Å)	Layer #
IIA	70	No pattern	Pb _{0.32} Zr _{0.53} Ti _{0.47} O ₃	400	1
			Pb _{0.46} Zr _{0.53} Ti _{0.47} O _{2.5} Si _{0.5}	400	2
			Pb _{0.36} Si _{1.0} O _{2.25}	800	3
			SiO ₂	20000	4
IIB	140	No pattern	Pb _{0.38} Zr _{0.53} Ti _{0.47} O ₃	950	1
			Pb _{0.38} Zr _{0.53} Ti _{0.47} O _{2.5} Si _{0.5}	400	2
			Pb _{0.36} Si _{1.0} O _{2.25}	2200	3
			SiO ₂	20000	4
IIC	390	Pyrochlore	Pb _{0.85} Zr _{0.53} Ti _{0.47} O ₃	3000	1
			Pb _{0.82} Zr _{0.53} Ti _{0.47} O ₃	200	2
			Pb _{0.71} Zr _{0.53} Ti _{0.47} O _{2.5} Si _{0.5}	400	3
			Pb _{1.4} Si ₂ O ₆	1000	4
			Pb _{1.2} Si ₂ O ₆	2000	5
			Pb _{1.0} Si ₂ O ₆	1200	6
			SiO ₂	10000	7

calculated. These are within 5% of those obtained from simulated spectra. No loss of Zr and Ti from the samples is observed. The discrepancy in total Pb concentration is less than 10% for films on quartz just as in the case of sapphire substrates. This Pb loss can be attributed to volatilization during heat treatment for both the

cases. For the individual layers in case of quartz substrates, simulation can provide only ratios of various elements and hence it is important to fix at least one ratio from some other argument. The initial simulations showed that Zr and Ti concentrations do not change after heat treatment. The insignificant amount of tailing towards the low energy ends of Zr and Ti peaks can be attributed to depth undulation at the interface. Therefore Zr/Ti ratio is fixed at the nominal composition (i.e. 0.53/0.47) and all other ratios are adjusted accordingly.

For the two relatively thinner samples on quartz, IIA and IIB, three layers had to be invoked in which top layer (layer 1) is only lead deficient while layer 2, in addition, shows presence of Si. The top two layers containing nominal Zr/Ti ratio add up approximately to the thickness of the film obtained by profilometer measurements. This shows that the inter diffusion of Pb and Si has occurred across the original interface between PZT layer and quartz substrate leading most probably to the formation of a lead silicate compound (e.g. PbSiO_3 or PbSi_2O_7). Layer 3 can then be viewed as arising out of lead silicate dispersed in quartz matrix. The presence of layer 2 in the structures of IIA and IIB is an indication that there is formation of lead silicate in PZT layer as well, spanning several hundreds of angstroms. In other words, lead silicate is dispersed on both sides of the original interface between PZT layer and the quartz substrate producing a structure consisting of three apparent layers corresponding to Pb deficient PZT (layer 1) mixture of PZT and lead silicate (layer 2) and lead silicate dispersed in quartz matrix (layer 3). The comparative thicknesses of layers 2 and 3 show that lead diffusion occurs deep into the substrate whereas the diffusion of Si into PZT layer is small.

The simulated structure for thicker sample IIC on fused quartz is similar except for the fact that the top PZT layer is subdivided into two layers (layers 1 and 2) and the intermediate layer into three layers (layer Nos 4, 5, 6) reflecting Pb gradient in the whole structure as would be expected for a diffusing species. Layer No. 3 as earlier, is to be viewed as a part of PZT layer containing lead silicate phase. In this case the top three layers correspond approximately to the as-deposited film. Recall that no XRD peak was observed for cases of thinner films on quartz substrate (samples IIA and IIB) suggesting that these films are amorphous. RBS results on these films show that the Pb deficiency in the top PZT layer is as high as 60%. This suggests that these films are amorphous because Pb deficiency is too high for crystallization to occur. However in the thicker pyrochlore film (IIC) the overall Pb deficiency is 15% in the top PZT layer. It is reasonable to conclude that this level of Pb deficiency allows only a pyrochlore phase to form. When the film thickness is larger than $1.5\text{ }\mu\text{m}$ the composition of the layer is nearly same as the nominal composition and gives rise to a perovskite phase—this has been checked by RBS results on such thick films. In contrast, in the case of sapphire substrates, Pb is neither consumed in any interfacial reaction nor it diffuses into the substrate. The marginal Pb loss in this case can be explained by losses due to evaporation from the surface. Therefore the perovskite phase forms in PZT layers on sapphire irrespective of thickness down to $450\text{ }\text{\AA}$. The existence of unusually long tail of Pb peak towards the low energy side is most probably due to some cracks that appear in the thicker films. This feature is absent in case of crack-free thinner films.

RBS results thus show that Pb diffuses readily from PZT film to a depth of several thousand angstroms into the quartz substrate during the annealing step. This

results in a film highly depleted in Pb. This deficiency in Pb, rather than any substrate (epitaxial) effect is believed by us to be responsible for the retention of the amorphous or pyrochlore phase in the films on quartz. On sapphire where no such diffusion is found to occur, the perovskite phase forms readily.

The other observed effect relating to the phase formation can similarly be explained in terms of Pb deficiency in the film. Thus in thicker film, even on quartz, a perovskite phase is obtained because the top layer, which is the layer sampled in X-ray diffraction, does not develop Pb deficiency because of its large diffusion distance from the substrate. High Ti content (low Zr/Ti ratio) also favours the perovskite formation because Ti binds Pb more effectively as revealed by much lower activity of PbO in PbTiO₃ than in PbZrO₃ (Klee *et al* 1992), the loss of Pb thereby is less in composition with lower Zr/Ti ratio.

4. Summary

The difficulty in the formation of the perovskite phase in PZT films under certain experimental conditions is directly related to the extent of Pb loss from the film. If the Pb loss is not significant, then the perovskite structure forms easily. This is the case, for example, for thin films on substrates such as sapphire, platinum etc where the only Pb loss mechanisms is the volatilization of PbO during annealing. When Pb is also lost due to diffusion into the substrate or due to reaction with the substrate then the film may become heavily deficient in Pb and will not transform to the perovskite structure. Such diffusion is found to be substantial for amorphous substrates such as quartz.

For using the ferroelectric PZT film in non-volatile memory application, it is desirable to integrate the film with Si semiconductor technology. In view of the high reactivity of Pb with Si, and consequent difficulty in the formation of perovskite phase, it would be necessary to develop suitable diffusion barrier layers between PZT film and Si substrate. Development of such barrier layer is one of the most important issues in utilizing PZT film in memory application.

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