

Growth of perovskite PZT and PLZT thin films

R. R. NEURGAONKAR, I. SANTHA, J. R. OLIVER, E. T. WU
Rockwell International Science Center, Thousand Oaks, California 91360, USA

L. E. CROSS
Pennsylvania State University, University Park, Pennsylvania 16802, USA

This paper reports preliminary results on the fabrication of perovskite PZT and PLZT thin films using a sputtering technique. For glass, quartz and sapphire substrates, it was necessary to raise the substrate temperature above 550°C to achieve perovskite tetragonal structures of interest. Growth at temperatures below 550°C yielded a major pyrochlore structure phase. Excess of PbO in the target was also required to maintain stoichiometry in these films.

1. Introduction

Recently, considerable attention has focused on the development of low-loss ferroelectric thin films for optical waveguides. Several attempts have been made to grow single crystal waveguide films using materials such as LiNbO₃ [1-3], PLZT [4-6], KLN and SBN [7, 8]. More recently, other ferroelectric materials such as BaTiO₃ and PBN have been considered using semiconductor substrates for various optical applications, including waveguides, spatial light modulators, switches and pyroelectric detectors. The top surfaces of as-grown LiNbO₃ and SBN films fabricated by liquid phase epitaxial growth, chemical vapour deposition, melting methods and so on, are relatively rough so that they must be optically polished to couple a light beam into the film. On the other hand, polishing is not necessary for sputtered thin films. Therefore, the sputtering technique has been used in the present work to develop perovskite PZT and PLZT films using a variety of substrates such as glass, quartz and sapphire. This paper reports the growth of PZT and PLZT films and their associated growth problems.

2. Experimental procedure

The sputtering targets employed were a mixture of PZT or PLZT and PbO. Approximately 5 mol% excess PbO was added in these targets to control the Pb concentration in the films. The targets were prepared using ceramic sintering or hot pressing; well-

mixed powders were cold pressed and then sintered or hot pressed at 1100°C after ball-milling.

Sapphire (Al₂O₃) and quartz (SiO₂) substrates were first etched by sputtering. The substrates were mounted on a heating block with a stainless steel mask of 0.2 mm thickness. Substrate temperature was monitored by a Pt-Pt.Rh 13% thermocouple inserted into the centre of the substrate holder. The sputtering conditions, summarized in Table I for each material, are as follows:

Target-substrate distance	5 cm
Input power density	1.9 to 2.4 W cm ⁻²
Sputtering gas	Ar:O ₂ (40:60 or 50:50)
Gas pressure	8 to 12 μm
Substrate temperature	300 to 600°C
Deposition rate	20 to 25 Å h ⁻¹
Annealing temperature	700 to 800°C

3. Experimental results and discussion

PZT and PLZT compositions have been of practical interest for the last 25 years and are being exploited for optical applications such as switches, modulators, image storage and optical display devices. PZT occurs on the pseudobinary PbZrO₃-PbTiO₃ system and exhibits a morphotropic phase boundary at a Zr:Ti ratio of 52:48, as shown in Fig. 1. However, the development of bulk single crystals has been hindered by growth problems associated with Pb²⁺ losses during growth and cracking when cycling through the

TABLE I Growth condition for PZT and PLZT films

Substrate	Substrate temperature		Atmosphere	Power density (W cm ⁻²)	Film thickness (μm)	Remarks
	≤ 550°C	~ 600°C				
PZT films						
Glass	Pyrochlore	Perovskite	50% Ar + 50% O ₂	2.2-2.4	1-5	
Quartz (SiO ₂)	Pyrochlore	Perovskite	50% Ar + 50% O ₂	2.2-2.4	3-10	Excellent films
Sapphire (Al ₂ O ₃)	Pyrochlore	Perovskite	50% Ar + 50% O ₂	2.2-2.4	3-10	Reasonable quality
PLZT films						
Glass	Pyrochlore	Perovskite	40% Ar + 60% O ₂	1.9-2.1	3-10	Reasonable quality
Quartz (SiO ₂)	Pyrochlore	Perovskite	40% Ar + 60% O ₂	1.9-2.1	2-8	Excellent quality
Sapphire (Al ₂ O ₃)	Pyrochlore	Perovskite	40% Ar + 60% O ₂	1.9-2.1	2-5	Reasonable quality

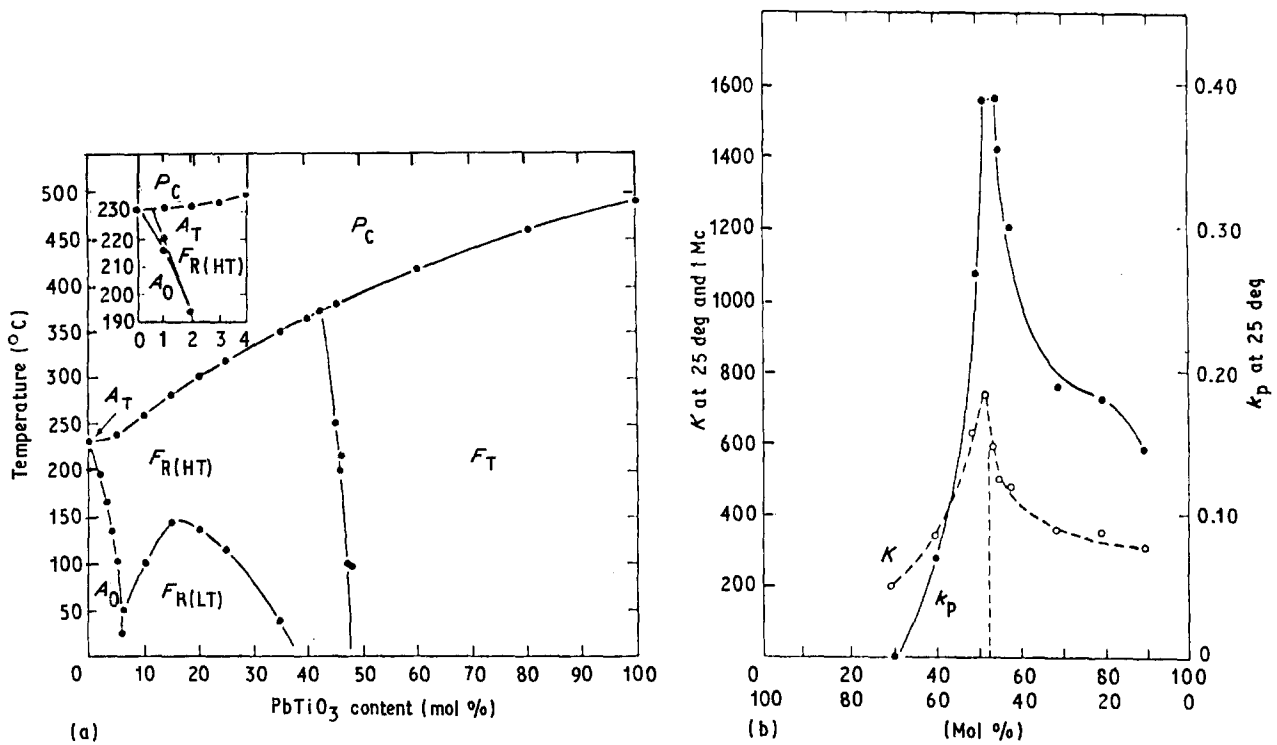


Figure 1 Morphotropic phase boundary in the PZT system.

paraelectric/ferroelectric phase transition. For this reason, thin-film growth of these compositions is now being explored in several countries [9-11].

The deposition of PZT and PLZT films by the sputtering technique has shown that the structure of the film is sensitive to the substrate temperature (Fig. 2). PZT or PLZT thin films having a pyrochlore structure were obtained below 550°C, whereas a perovskite structure was obtained above 600°C. However, traces of $PbTi_3O_7$ were observed with Pb^{2+} deficiencies, and for this reason, an extra 5 mol % PbO was incorporated in the targets to stabilize the film composition.

Fig. 3 shows the X-ray diffraction patterns of PLZT films sputtered on fused quartz and sapphire and for a PLZT(9/65/35) hot-pressed ceramic. In Fig. 3, (a) is for a film (~4 μm thickness) sputtered at a substrate temperature of 550°C with a target containing 5 mol % of PbO excess, (b) is for a film sputtered at 600°C with a target containing 3 mol % PbO excess, and (c) is for the hot-pressed PLZT ceramic target.

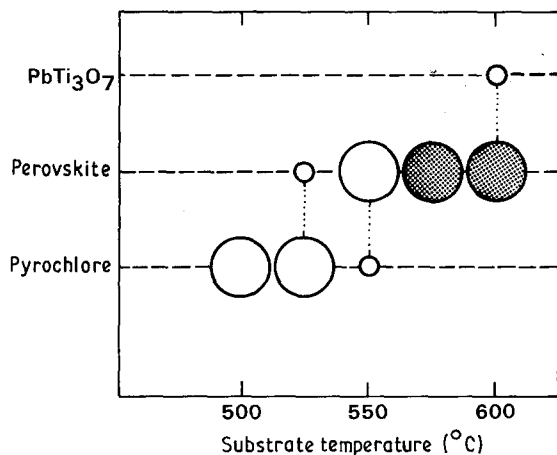


Figure 2 Structural sensitivity of PZT and PLZT compositions.

The good agreement between the thin film and ceramic target patterns shows that the films have maintained the desired perovskite structure, although they are polycrystalline due to the poor lattice match with the substrates. A small split of the (200) peak into (200) and (002) was observed after a post-growth anneal at 700°C/2h, indicating a tetragonal symmetry. However, this caused some loss of Pb^{2+} , as indicated by the appearance of small second phase peaks associated with ZrO_2 . To maintain a perovskite phase during growth, substrates were held at 600–650°C; growth temperatures below 350°C resulted in completely amorphous films which could not be annealed to a crystalline form. Although excess PbO is clearly required to maintain film stoichiometry during growth, based on evidence from this work and the results of others [1], the optimum excess PbO amount still needs to be established.

4. Future planned work: multilayered ferroelectric films

Recent work by Higuma *et al.* [12] has shown that the growth of PLZT single crystal films is possible using

TABLE II Lattice match between PZT/PLZT and tungsten bronze substrates

Film composition	(001)-oriented tungsten bronze substrates			Perovskite $SrTiO_3$
	SBN:60	BSKNN	PBN:60	
PZT (40:60)				
$a = 4.042 \text{ \AA}$	2.6%	1.99%	1.4%	3.01%
$c = 4.082 \text{ \AA}$	3.6%	3.00%	3.00%	4.12%
PLZT (8/40/60)				
$a = 4.029 \text{ \AA}$	2.1%	1.5%	1.1%	2.5%
$c = 4.072 \text{ \AA}$	3.4%	2.7%	2.1%	4.3%
PBN:60				
$a = 12.501 \text{ \AA}$	0.38%	0.20%	-	-
$c = 3.985 \text{ \AA}$	0.65%	0.35%	-	-

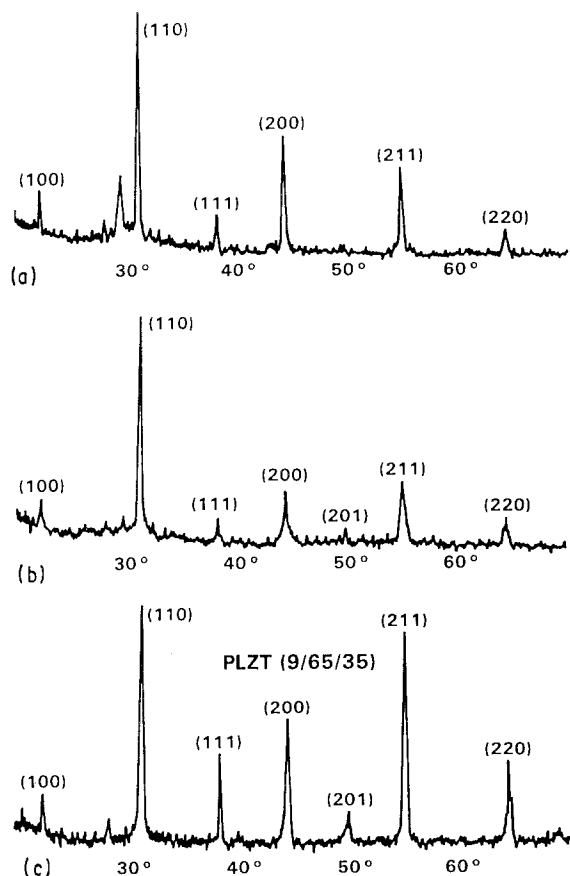


Figure 3 X-ray diffraction patterns of PLZT sputtered films and hot-pressed ceramic. (a) Film sputtered with a target with 5 mol % excess PbO; (b) film sputtered with a target with 3 mol % excess PbO; and (c) hot-pressed ceramic.

perovskite SrTiO_3 substrates at temperatures between 500 and 700°C. Although film growth was successful, there was a considerable lattice mismatch between the film and the substrate. Table II summarizes the lattice match of PLZT with SrTiO_3 and other ferroelectric crystals, including tungsten bronze SBN and PBN. The lattice match between PLZT and PBN is very good for (001)-oriented PBN and potentially allows the growth of better quality PLZT films. In future work, we propose to develop PZT and PLZT films as follows.

1. SBN:60 substrate with a 5 μm PBN:60 film for lattice matching to PZT or PLZT.

2. SBN:60 substrate with a 5 μm PBN:60 film and then alternate PLZT and PBN layers to develop a superlattice structure.

Since the lattice mismatch between PLZT and PBN is small, we expect that optical-quality PZT/PLZT

films or PLZT-PBN superlattices can be more readily achieved with these film structures. An additional advantage is the ability to improve the lattice match by adjustment of the Pb:Ba ratio in PBN and thereby improve PZT/PLZT film crystallinity.

The previously discussed considerations for the electrical evaluation of PBN:60 thin films also apply here in the case of PZT/PLZT films. Because of the additional complexity of PZT/PLZT thin-film growth, the growth of good quality films on metallized substrates may be vastly more difficult than for PBN:60. A closely spaced surface electrode configuration appears to be a preferable geometry for electrical characterization of PZT/PLZT films, at least in the near term. A high-temperature sample holder to accommodate this type of geometry for d.c. conductivity, pyroelectric and dielectric measurements over a wide temperature range is now being designed and tested for this purpose.

Acknowledgement

This work was supported by the AFOSR (Contract No. F49620-86-C-0052) and ONR (Contract No. N00014-81-C-0463). The authors are grateful for the discussions on this research with W. F. Hall and T. McGill (Caltech).

References

1. A. OKADA, *J. Appl. Phys. Lett.* **48** (1977) 2905.
2. M. ISHIDA, S. TSUJI, K. KIMURA, H. MATSUNAMI and T. TANAKA, *J. Cryst. Growth* **45** (1978) 393.
3. M. ADACHI, T. SHIOSAKA and A. KAWABATA, *Ferroelectrics* **27** (1980) 89.
4. Y. HIGUMA, K. TANAKA, T. NAGAWA, T. KARIYA and Y. HAMAKAWA, *Jpn J. Appl. Phys.* **16** (1977) 1707.
5. M. ISHIDA, T. TSUJI, K. KIMURA, H. MATSUNAMI and T. TANAKA, *J. Cryst. Growth* **45** (1978) 383.
6. H. ADACHI, T. KAWAGUCHI, K. SETSUNE, K. OHJI and K. WASA, *Appl. Phys. Lett.* **42** (1983) 867.
7. T. SHIOSAKI, M. ADACHI and A. KAWABATA, *Thin Solid Films* **96** (1982) 129.
8. R. R. NEURGAONKAR and E. T. WU, *Mat. Res. Bull.* **22**(8) (1987) 1095.
9. C. A. T. SALAMA and E. SICIUNAS, *J. Vac. Sci. Technol.* **9** (1971) 91.
10. T. NAGAMOTO, T. KOSAKA, S. OMORI and O. OMOTO, *Ferroelectrics* **37** (1981) 681.
11. S. IIDA and S. KATAOKA, *Appl. Phys. Lett.* **18** (1971) 391.
12. Y. HIGUMA, K. TANAKA, T. NAGAWA, T. KARIYA and Y. HAMAKAWA, *Jpn J. Appl. Phys.* **16** (1977) 1707.

Received 25 November 1987

and accepted 3 March 1988