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The optical waveguide characteristics of highly orientated sol–gel derived polycrystalline ferroelectric PZT thin films

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Abstract

PZT ferroelectric thin films were deposited on various substrates by the sol–gel method. The close relationship between structure and refractive indexes was studied. The optical propagation losses of thin films were measured using the prism-waveguide coupling technique. The optical propagation loss of the films derived on SiO_2/Si (111) substrates is increased by increasing the heat treatment temperature. The optical propagation loss is not significantly increased at increased coating thickness. Epitaxial PZT thin films on $SrTiO_3$(l00) single crystal substrate had a single (001) orientation and showed optical propagation loss as small as 14.2 dB/cm at 632 nm. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sol–gel processes; D. PZT; E. Substrate; Orientation; Optical propagation loss

1. Introduction

Thin ferroelectric films such as PT, PZT, PLT, PLZT are excellent active optical materials in addition to a variety of potential electronic device application, due to their superior optoelectronic properties. These applications combine the unique properties of ferroelectric materials with the design flexibility of thin film geometries. Thin films application include thin film capacitors, micro-actuators, optical waveguide devices, optical memories and spatial light modulators [1–3].

The development of optical thin films for waveguide applications will enable a variety of new and highly useful optoelectronic functions [2,3]. Properties such as polycrystallinity, surface topography, and refractive-index homogeneity can affect the performance of optical thin film waveguides to a much greater extent than in other thin films applications, because of the long optical interaction lengths. Even a small degree of polycrystallinity in anisotropic media [4–6], for example, can be a significant source of optical scattering. Films of highly oriented crystalline structures with useful optical properties have been demonstrated [7–10].

Chemically prepared thin films are receiving increased attention for their electrical and optical properties [4–10]. PZT thin-film integrated with Si and other substrates have several applications, such as optical waveguides and spatial light modulators. Using sol–gel process methods, we have prepared crystalline, transparent and crack-free thin films of several lead-based ferroelectrics on a variety of substrates. These films are of suitable thickness to permit optical waveguiding of visible light.

Sol–gel derived oriented and epitaxial thin films have been reported [8,9,11–13] for PZT ferroelectric materials. Few studies have involved the preparation and properties of sol–gel derived PZT oriented and polycrystalline thin films. In the present study, we produced PZT (50/50) thin films prepared on SiO_2/Si, $SrTiO_3$ (100) and fused-quartz substrates through the sol–gel method. Relationships between thin film structure, preparation technique and waveguide properties are reported. Optical loss and orientation of thin films were also examined.

The crystalline phases of the thin films were characterized by X-ray diffraction (Rigaku D/max 2400). The refractive indexes of the films deposited on Si(111) and Pt/Ti/SiO_2/Si (111) substrates were measured using ellipsometry at 632.8 nm wavelength. The morphology, structure and surface roughness were observed by atomic force microscopy (Digital NanoScope IIIa).

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2. Experimental procedure

The starting metal–organic materials were lead acetate hydrate $Pb(CH_3COO)_2{\cdot}3H_2O$, $ZrO(C_7HO_{13}O_2)_2$ and titanium butoxide, $Ti(OC_4H_9)_4$. 2-Methoxyetanol ($CH_3OCH_2CH_2OH$) was the solvent. $Pb(CH_3COO)_2{\cdot}3H_2O$ was dissolved in 2-methoxyetanol and continuously heated at 118°C for 10 min in order to remove the water. The dehydrated solution was cooled to 50°C before $ZrO(C_7H_{13}O_2)_2$ and titanium butoxide $Ti(OC_4H_9)_4$ were added. The solution was raised to 118°C in order to promote complexation. Finally, acetyl acetone (Ti: AcAc = 1:1 mol) was added to form the stock solution. The concentration of the final solution was 0.5 M.

SiO_2/Si (111), $SrTiO_3$ (100), Pt/Ti/SiO_2/Si (111) and fused-quartz (with a thickness of SiO_2 1000 nm, Ti 40 nm, Pt 200 nm) substrates were used for spin coating in a class 100 clean room. After the spin-coating deposition, the gel films were fired at various temperatures in an infrared furnace. The samples were fired at 400°C for 2 min, at other temperatures for 30 mm. Thick films were produced by a multiple coating technique. The thickness of the fired sample is about 90 nm for one coating.

3. Results and discussion

3.1. Crystalline phase deposited on different substrates

Fig. 1 shows the X-ray diffraction spectra derived on Pt/Ti/SiO_2/Si (111) substrates. The pure perovskite phase was obtained at the highest heat treatment temprature.

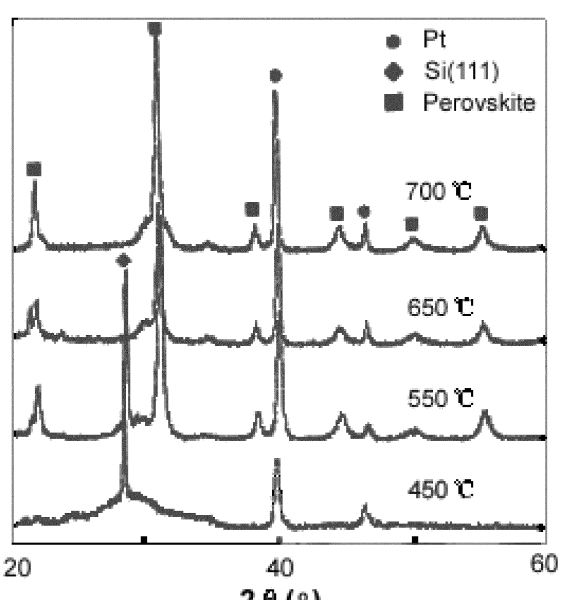

Fig. 1. XRD spectra of thin films prepared on the Pt/Ti/SiO_2/Si (111); ▲ perovskite, ■ pyrochlore, ● Pt.

Fig. 2 shows the XRD spectra of thin films deposited on different substrates. The films formed the perovskite phase on Pt/Ti/SiO_2/Si (111) substrates, whereas the films deposited on SiO_2/Si (111) and fused-quartz substrates formed the pyrochlore and the perovskite phase. The content of the perovskite phase in films heat treated at 550°C is higher than for films heat treated at 450°C deposited on fused-quartz substrates.

PZT thin films crystallized on $SrTiO_3$ (100) substrates showed (001) orientation without any misoriented planes or pyrochlore phases, according to XRD patterns (Fig. 3).

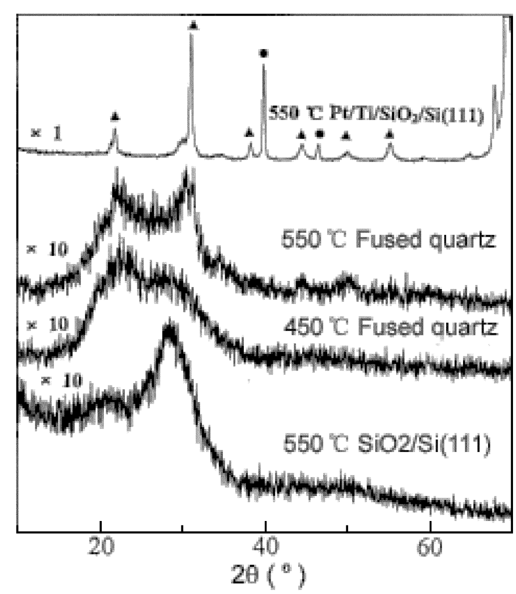

Fig. 2. XRD spectra of thin films derived on various substrates.

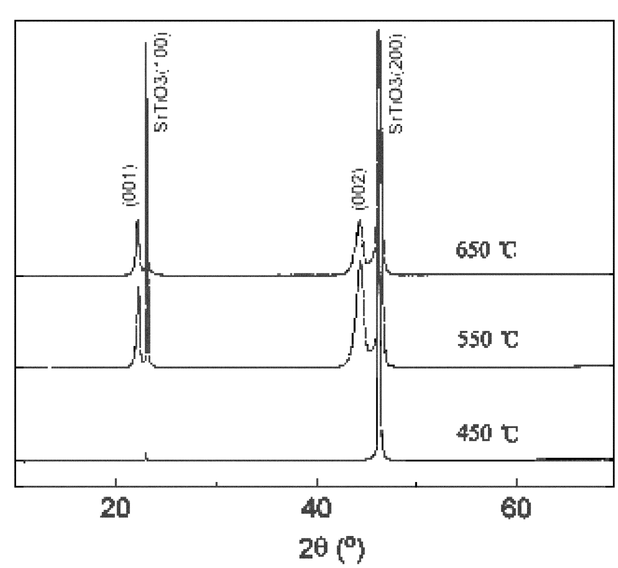

Fig. 3. XRD patterns of thin film prepared on the $SrTiO_3$(100).

3.2. Relations of refractive index and structure

The refractive indexes of the films deposited on Si (111) and $Pt/Ti/SiO_2$ (111) substrates increase with increasing heat treatment temperature, reflecting the effect of film densification (Table 1). At 500–600°C for films deposited directly on Si, the index begins to decrease. This decrease is due to interfacial reactions at the PZT–Si interface leading to the formation of SiO_2 and/or lead silicate species [14]. When the films are deposited on platinized wafers, the index continues to increase significantly above 500°C.

3.3. Optical propagation loss

Atomic force micrographs of PZT 50/50 thin films annealed respectively at 500 and 600°C are given in Fig. 4. Fig. 4(b) shows that two circular rosettes develop from their surrounding nanoscale pyrochlore matrix and there is a core at each rosette center [14,15]. The surface roughness (Table 2) for these perovskite rosettes and the matrix are 2.46 and 0.60 nm. Fig. 4(d) shows the AFM picture of the perovskite phase inside a rosette structure, which has grain size of about 40–80 nm. It has been reported [16] that PZT amorphous films form the pyrochlore phase below 500°C, and then the pyrochlore phase is converted to the PZT equilibrium perovskite phase at higher temperature in a slow kinetic process.

The arrangement for attenuation measurement of the thin films is shown in Fig. 5. The optical propagation loss was verified by measuring the scattered light from the transmitted light beam as a function of the propagation distances shown in Tables 3 and 4.

Tables 3 and 4 show the relationship among the optical propagation loss, the heat treatment temperature, and the layer number of epitaxial PZT films prepared on SiO_2/Si (111) substrates, respectively. The optical propagation loss increased rapidly with increasing heat

Table 1
Refractive indices of the films vs heat treatment temperature

Heat treatment temperature (°C)	200	500	550	600
Refractive index (Si (111))	1.73	1.78	1.70	1.71
Refractive index ($Pt/Ti/SiO_2/Si$ (111))	–	1.95	2.04	–

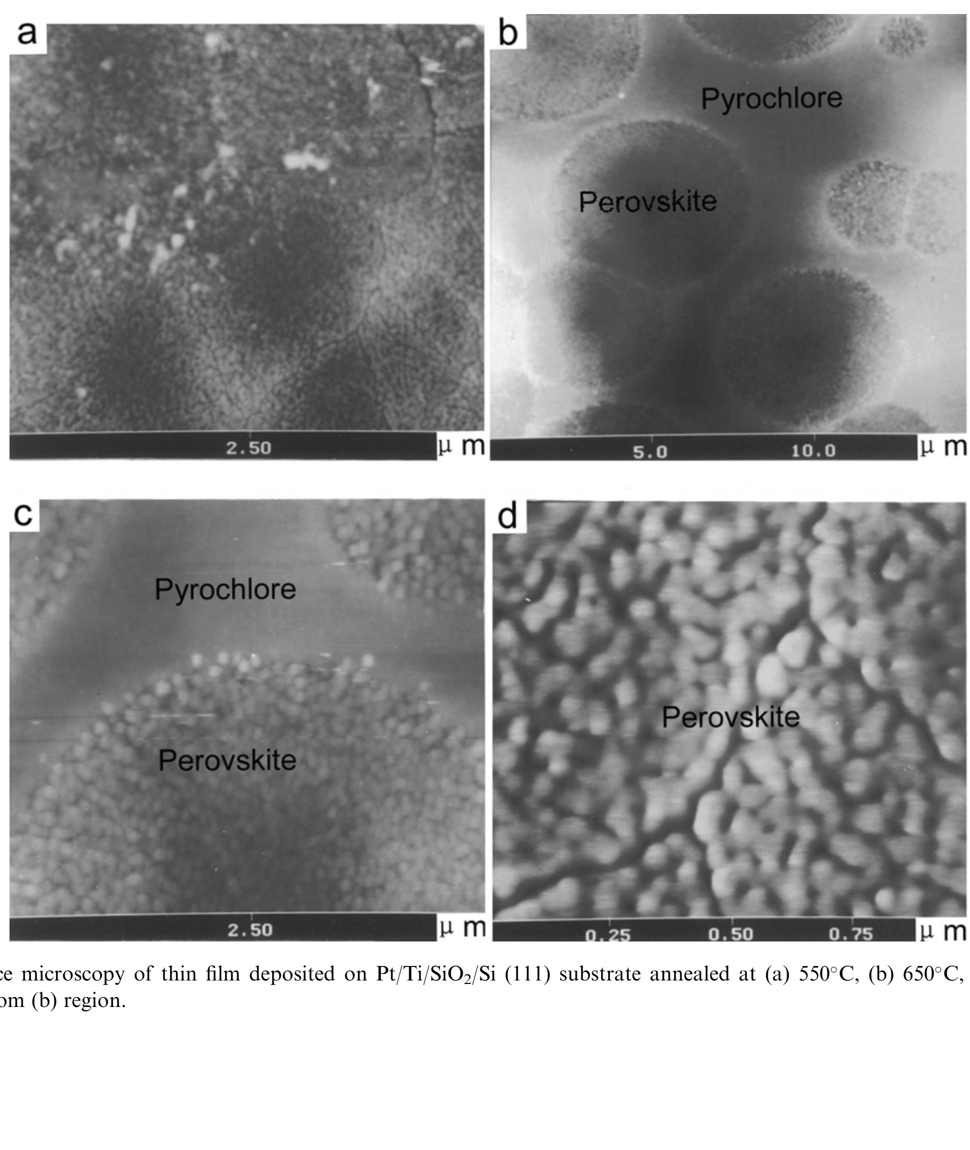

Fig. 4. Atomic force microscopy of thin film deposited on $Pt/Ti/SiO_2/Si$ (111) substrate annealed at (a) 550°C, (b) 650°C, (c) and (d) enlarged perovskite grains from (b) region.

Table. 2
Relations of heat treatment temperature and surface roughness (PZT/Pt/Ti/SiO_2/Si)

Heat treatment temperature	400°C	500°C Pyrochlore	500°C Perovskite	600°C
Surface roughness (nm)	0.325	0.601	2.461	4.02

Table 3
Relations of heat treatment temperature and surface scatter loss (PZT/SiO_2/Si) (two layers, thickness 180 nm)

Heat treatment temperature (°C)	400	500	600
Surface roughness (nm)	0.331	1.39	0.589
Interaction length (μm)	0.505	0.168	0.505
Optical propagation loss (dB/cm)	20.4	33.1	39.1
Surface scatter loss (dB/cm)	1.75	4.41	1.91
Body loss (dB/cm)	18.6	29.1	36.6

Table 4
Relation of optical propagation loss and layer number

Layer number (400°C, 30 min)	1	2	3
Optical propagation loss (dB/cm)	17.9	20.4	23.7

treatment temperature. Table 4 shows the optical propagation loss for the PZT thin film to increase slightly with increasing coating thickness.

There are several sources of loss, such as absorption, leakage, internal scattering, surface scattering and interface scattering [6]. Among these sources, internal scattering and surface scattering seemed to have the major influence in the present case. The surface scatter loss is calculated from the surface roughness [17]. The above results show that internal scattering was dominant rather than surface scattering. In order to lower internal scattering, highly oriented PZT thin films are needed [8]. Table 5 shows the optical propagation loss of thin films prepared on $SrTiO_3$ (100) single crystal. The optical propagation loss for PZT thin film prepared on $SrTiO_3$ (100) substrate at 600°C was 14.2 dB/cm, which was smaller compared to 39.1 dB/cm for the PZT thin film prepared on SiO_2/Si substrate.

Table 5
Relations of optical propagation losses and heat treatment temperatures for PZT prepared on $SrTiO_3$ (100) single crystals

Heat treatment temperature (two layers)	500°C	550°C	600°C
Surface roughness (nm)	0.42	0.85	1.45
Optical propagation loss (dB/cm)	26.5	21.4	14.2

Epitaxial PZT on $SrTiO_3$ had a single (001) orientation, and a smooth surface. The optical propagation loss was as small as 14.2 dB/cm at 623 nm. Thin films deposited on $SrTiO_3$ (100) substrate are different from those deposited on SiO_2/Si (111). The optical propagation loss of thin films decreases with increasing heat treatment temperature although surface roughness increased. The small amount of residual amorphous phase and/or pyrochlore phase, that were hard to verify by means of XRD, may be one of the cause of the internal scattering. There was an amount of residual amorphous phase and pyrochlore phase in thin films deposited on SiO_2/Si and fused quartz substrates. The highly oriented and crystallized PZT thin films reduce internal scattering.

Grain boundaries in optically anisotropic media may induce refractive index discontinuities among grains that can scatter the guided mode. Any polycrystalline medium that is not optically isotropic will scatter light if the crystalline orientation varies among grains. A refractive index at a grain boundary will therefore refract the propagating light at an angle given by Snell's law and effectively scatter the light at an angle from the direction of propagation. The nature and degree of scatter will depend on the statistics of grain orientation.

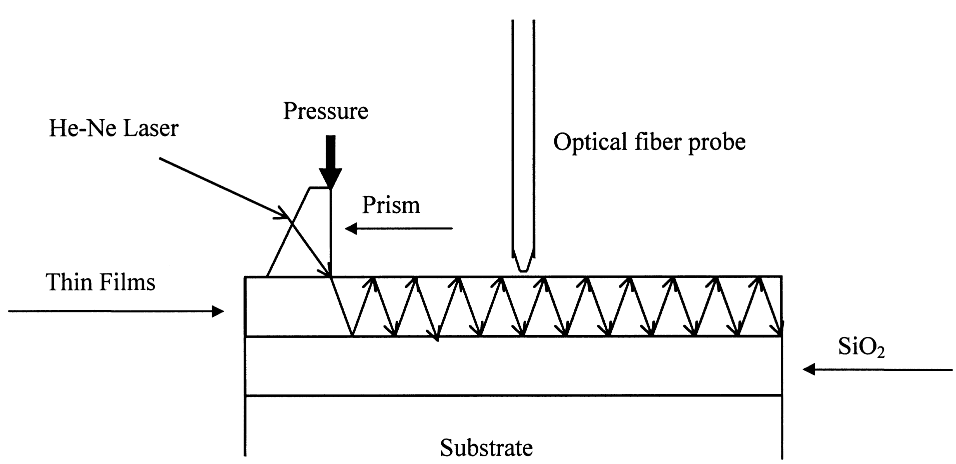

Fig. 5. Arrangement of the attenuation measurement for thin films.

4. Conclusions

Thin films of PZT (50/50) have been deposited by the sol–gel process on different substrates. The degree of crystallization is different from thin films deposited on different substrates. The refractive index of the prepared film is related to its structure. The optical propagation loss of the films derived on SiO_2/Si (111) substrates is increased with increasing heat treatment temperature. At increased coating thickness the optical propagation loss is not significantly increased. Epitaxial PZT thin films on $SrTiO_3$ (100) single crystal substrate had a single (001) orientation and showed optical propagation loss as small as 14.2 dB/cm at 632 nm.

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