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Deposition of PZT Thin Film and Determination of Their Optical Properties

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Abstract

The RF magnetron sputtering technique was applied for the thin film deposition. Hot-pressed PZT ceramics doped mainly with Bi and Ge were used as a target. The PZT thin films were grown on different substrates (Si, stainless steel and glass) and the sputtering parameters were optimised to assure the composition transfer between the target and the thin film. The obtained samples were analysed first as made and then after post deposition annealing. Structure of the films was investigated by X-ray diffraction. Optical properties of the thin films were investigated by: (i) linear absorption method and (ii) Raman scattering. Results of the modelling of the optical spectra for the PZT films on glass substrates are also reported. © 1999 Elsevier Science Limited. All rights reserved

Keywords: RF magnetron sputtering, films, X-ray methods, optical properties, PZT.

1 Introduction

There is a considerable interest in ferroelectric thin films, particularly in the lead–zirconate–titanate (PZT) system for their potential applications in microelectronics and microstructure technology today. In particular, the thin PZT films are very promising for application as ferroelectric memories[1,2] active optical waveguides and optical modulators,[2] high dielectric capacitors and non-linear capacitors,[3] microactuators,[4] pyroelectric sensors and sensor arrays,[3–6] piezoelectric sensors of dynamical deformation,[7] ferroelectric gate FET transistors,[8] and many others.[9]

The reported methods to form PZT films include, among others, sputtering, electron beam deposition, ion beam deposition, pulsed laser deposition, sol–gel process, metalorganic decomposition (MOD), and metalorganic chemical vapour deposition (MOCVD). Of all the reported techniques, the RF magnetron sputtering technique appears to be promising because it offers the advantages of high deposition rates, film uniformity, composition control, high film densities and compatibility with integrated circuit technology.[10]

It was our goal in the present study to deposit the PZT films on various substrates (glass, Si, stainless steel) and investigate their structure and optical properties by means of linear absorption method and Raman scattering. An attempt to model the optical spectra of the as-deposited PZT films on glass substrates was undertaken.

2 Experimental

The PZT-type thin films (in the range of 0·2–4 μm) have been prepared using RF magnetron sputtering with a hot-pressed ceramic target of nominal composition $Pb_{0\cdot97}(Zr_{0\cdot52}Ti_{0\cdot46})O_3$ doped mainly with Bi, Ge and known as PZT-89G.[11] The industrial vacuum system Alcatel SCM-650 equipped with the customised magnetron gun was used. The substrates are (001) Si wafers, stainless steel (AISI 304-type stainless steel) as well as glass. The sputtering conditions of PZT are shown in Table 1.

The two-stage method of the thin film growth was applied, namely: (i) deposition at temperature up to 500°C and (ii) post-deposition annealing in air atmosphere at temperatures within the range 600–650°C for 120 min. After annealing, the crystalline structure of the films was examined by X-ray diffraction.

Optical absorption spectra were measured by Shimadzu UV-3101 PC double beam spectrometer

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at room temperature. Raman scattering measurements were carried out in a back scattering geometry using a Raman Jobin-Yvon T64000 commercial system with an Olympus BH2-UMA microanalysis system with a CCD detector. The spectra were obtained at room temperature using 514 nm line generated by argon laser (Coherent Inova 92 Ar^{+}). The peak frequencies are accurate to better than 3 cm^{-1}.

3 Results and Discussion

In general, as-deposited films are amorphous and post-deposition annealing is needed to transform the film from the amorphous structure to the desirable ferroelectric–perovskite phase. The amorphous structure will first transform into an intermediate pyrochlore phase and then the pyrochlore phase will transform into the perovskite phase at a higher temperature.[12]

In the present study the perovskite type PZT target with tetragonal structure was used. It was characterised by the following parameters of the elementary cell: $a_T = 4{\cdot}039$ nm and $c_T = 4{\cdot}140$ nm. The X-ray diffraction pattern (using CuK_α radiation) of the target is shown in Fig. 1. X-ray diffraction results show that when the thin film was obtained at temperatures lower then 400°C, no definitive peak was observed and the film remained amorphous. As the deposition temperature increased to 400°C, two broad pyrochlore peaks were found at 2Θ of 29·4° and 34·4° as well as the perovskite peak at the 2Θ of 31·2°. The formation of a perovskite phase was observed after annealing in a furnace at temperatures within the range 600–650°C. X-ray diffraction spectra discussed above are shown in Figs 2 and 3. An X-ray diffraction pattern of the as-deposited PZT film grown on Si substrate at 400°C is presented in Fig. 2. Figure 3 shows the X-ray diffraction pattern of the PZT thin film grown on a stainless steel substrate at 150°C and further annealed at 650°C in a furnace for 2 h.

A Raman spectrum for the 4 μm thick PZT film deposited on steel at temperature of 150°C and annealed at 650°C for 2 h is shown in Fig. 4. The spectrum contains six peaks and one shoulder at about 500 cm^{-1}. Identification of the frequency peaks was performed on the basis of the published literature data[13] and the results are in good agreement with those reported for PZT films with tetragonal structure.

For weakly absorbing films on transparent glass substrates, transmission spectra (Fig. 5) contain information concerning the frequency dependent

Table 1. Sputtering conditions for PZT deposition

Target diameter	42×10^{-3} m
Target–substrate spacing	$(13–65)\times10^{-3}$ m
Sputtering gas	oxygen or argon–oxygen mixture
Base pressure	10^{-4} Pa
Power density	$(8{\cdot}5–22)\times10^{4}$ W m^{-2}
Gas pressure	0·2–4 Pa
Deposition rate	$(3–10)\times10^{-9}$ m min^{-1}

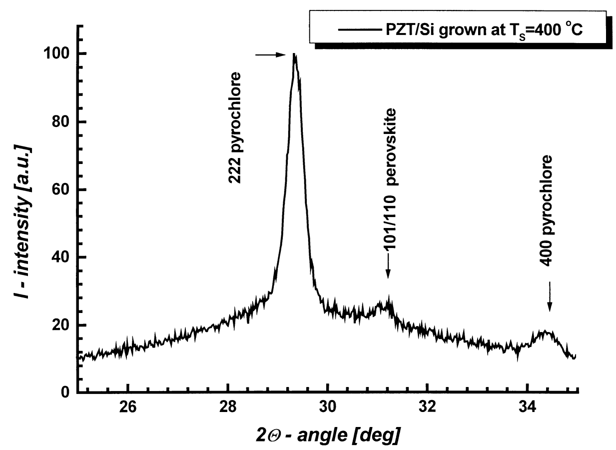

Fig. 2. X-ray diffraction pattern of the as-deposited PZT film on Si substrate.

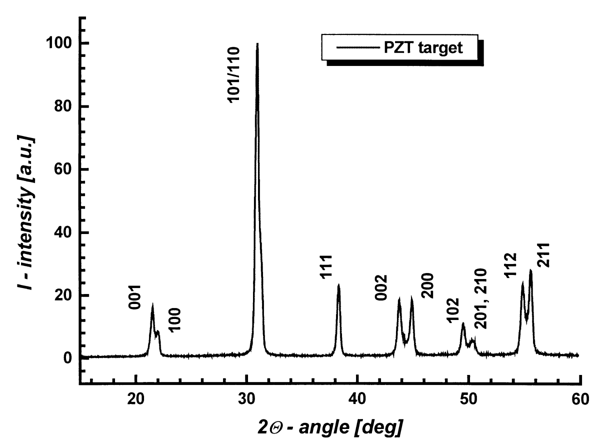

Fig. 1. X-ray diffraction pattern of the PZT target used for sputtering.

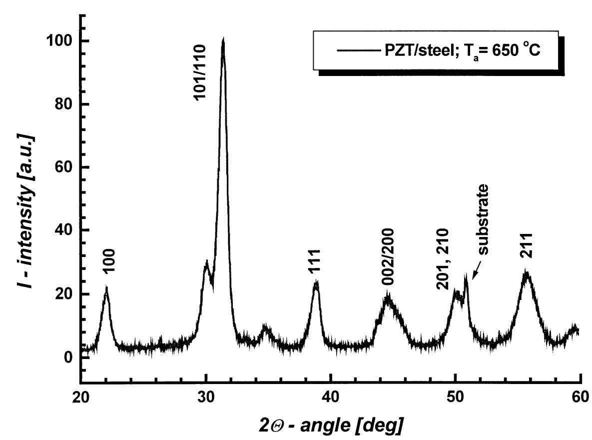

Fig. 3. X-ray diffraction pattern of the PZT film on stainless steel substrate annealed at 650 °C.

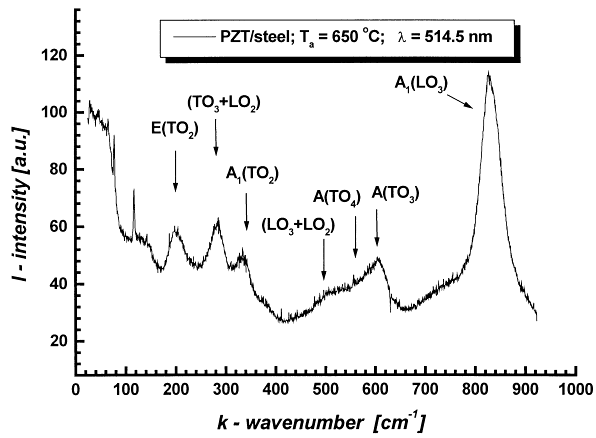

Fig. 4. Raman spectrum of the PZT film grown on stainless steel substrate at 150 °C and annealed at 650 °C for 2 h.

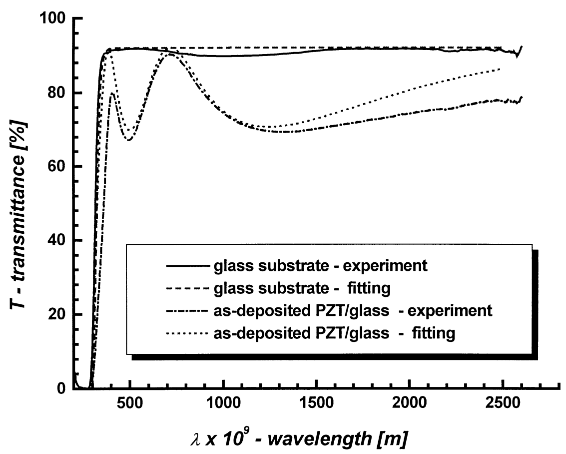

Fig. 5. Transmission spectra of the as-deposited PZT films on glass substrates.

dielectric function ε^* of PZT. First, we fitted the refractive index and the absorption edge energy of the glass, with $n_g = 1{\cdot}8$ and $E_g = 5{\cdot}35\,\mathrm{eV}$, respectively. Secondly, to model ε^* of PZT, we assumed a direct band structure[14] and some disorder producing a Gaussian distribution of the absorption edge energy E_g in PZT. Three parameters were adjusted in this calculation: the transition strength, the standard deviation of the E_g distribution and the background dielectric constant. They were chosen to reproduce the dependence of the refraction and extinction coefficients upon energy, which was already published.[14] To take into account the voids, we used the modified Maxwell–Garnett approach[15] considering the packing density as a fitting parameter. Given the complex dielectric function of the film and the substrate we calculated the optical spectra of the whole structure. This has been done using the standard expressions for the reflectivity and transmittance of a slab (of PZT) placed between two semi-infinite media (air and glass). The only additional parameter required for this is the film thickness, which was measured independently.[16] The measured and calculated

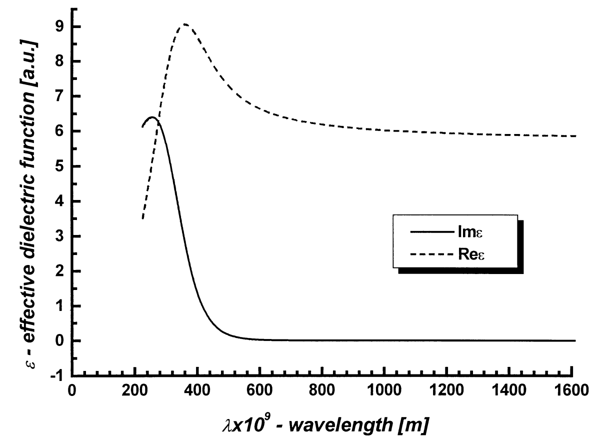

Fig. 6. Effective dielectric function for as-deposited PZT film on glass substrate.

transmission spectra of the as-deposited PZT film on glass substrate are shown in Fig. 5. The calculated effective dielectric function for PZT ($x = 0{\cdot}52$, fitted packing density 0·9) is shown in Fig. 6.

4 Conclusions

Thin films of lead–zirconate–titanate have been deposited by RF magnetron sputtering on different substrates. X-ray measurements showed that as-deposited films had pyrochlore type structure. Thermal processing conditions of 600–650 °C and 2 h were required for the formation of perovskite structure. The Raman scattering spectrum of the PZT thin film deposited on stainless steel was in good agreement with literature data. Mathematical processing of the transmission spectra allow us to calculate effective dielectric function for PZT thin films.

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