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Growth of $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films on (111) silicon substrates

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$Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films were successfully grown on (111) silicon substrates by a high oxygen pressure RF sputtering technique which is used for the preparation of high Tc superconductors (HTS) thin films. Intermediate Ti and Al layers were evaporated on the (111) oxidized Si wafers and then subjected to an annealing processes in a furnace at 500ºC, 550ºC and 600ºC, for 5 hours before the ferroelectric thin film was deposited. The influence of the substrate preparation and deposition conditions on the structural properties of these films were examined by scanning electron microscopy (SEM) and x-ray diffraction (XRD) analysis.

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1. Introduction

PZT films are of great interest, mainly because of the possibility of using them in several applications, such as: nonvolatile memories [1,2], optical waveguide devices [3], pyroelectric detectors [4,5], tunable microwave devices [6,7], and others. Applications, however, require materials that are uniform in chemical composition and physical structure, thus systematic studies on the deposition of PZT thin films are essential for improving the crystalline quality of these films.

A wide variety of physical and chemical deposition techniques have proved successful in the fabrication of high-quality PZT films [8, 9, 10]. Here we report the growth of PZT thin films by a high oxygen pressure RF sputtering technique [11]. The principal characteristic of this technique is that the working gas is pure oxygen at pressures near 1 torr. The structural characteristics of PZT thin films fabricated by this method are analyzed.

2. Experimental procedure

The substrates were n-type (111) silicon 2” diameter wafers with a diffused SiO_2 layer. The Ti and Al layers were deposited by e-beam evaporation with the substrate at room temperature. To improve the film quality we found necessary to perform an annealing process on the Ti-Al layers. The annealing temperatures were the same as the deposition temperatures, that is: 500ºC, 550ºC and 600ºC, for 5 hours. The characteristics of the prepared substrates are summarized in the Table I.

The overall sputtering conditions of PZT are summarized in Table II. Targets were prepared from PbO, TiO_2 and ZrO powders, with 10%wt. excess PbO.

Phases and crystalline structures of the films were determined by XRD. Morphology surface and micro-composition was studied by SEM and energy dispersion spectroscopy (EDS).

Table I. Summary of substrate characteristics

Substrate	(111) Silicon wafer 2” ϕ
SiO_2 layer	~ 100 nm
Ti layer	~ 50 nm
Al layer	~ 100 nm
Annealing temp.	500ºC, 550ºC, 600ºC
Annealing time	5 hrs

Table II. Sputtering condition of PZT thin film

Target	$Pb(Zr_{0.53}Ti_{0.47})O_3$
Gas composition	O_2 100%
Gas pressure	0.7 - 1 torr
RF power density	2 - 3 W/cm^2
Substrate - target distance	50 mm
Substrate temperature	500°C – 600ºC

3. Results and discussion

XRD pattern for the oxidized Si substrates with Ti and Al layers before and after the annealing process are shown in Figure 1. The pattern for the unannealed substrate shows only the Si, Ti and Al peaks as expected. On the other hand, the pattern for the annealing substrate reveals a new peak corresponding to a Ti-Al oxide while the Ti and Al peaks have disappeared. It indicates that the Ti and Al have interdiffused and oxidized during the annealing process.

Figure 2 is a representative XRD pattern of a PZT film deposited on a substrate on which no thermal treatment was applied previous to the deposition. It can be observed that whilst the peaks coming from Si and Ti-Al oxide are clearly defined, this is not true for the PZT peaks.

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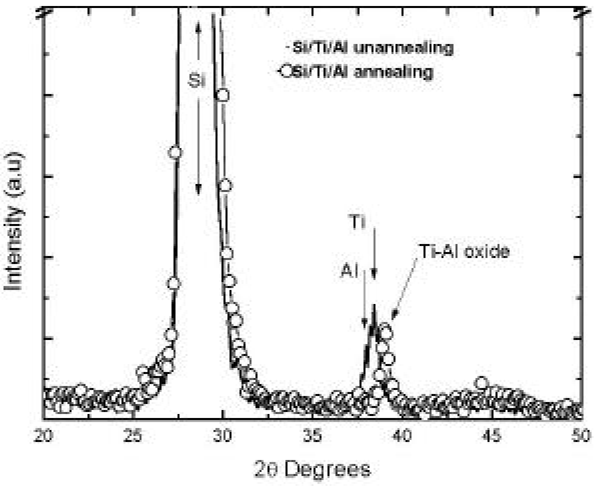

Figure 1. X-ray diffraction patterns of Si substrates with Ti and Al layers before and after annealing process

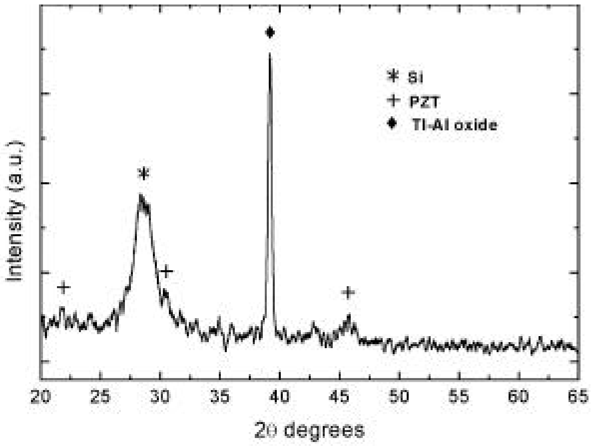

Figure 2. X-ray diffraction pattern of PZT film deposited on a substrate without thermal treatment.

The XRD patterns for PZT films deposited on unannealed and annealed substrates indicate an improvement in the structural characteristics of the films when are grown on annealed substrates. Figure 3 shows the evolution of the intensity of the PZT films peaks as the annealing temperature were increased from 500°C to 600°C. The films has a perovskite phase and micro-crystalline structure having (110) and (011) preferential orientations. Notice that the peaks corresponding to the Ti-Al oxide remain unchanged.

The surface morphology of films as observed by SEM, is shown in Figure 4. The surface is basically flat and smooth. The detailed observation of the surface in back-scattering mode reveals the presence of several circular zones with approximately 10μm in diameter (Figure 5).

The low-energy part of EDS spectrum over these zones (Figure 6a) indicates that this zone is richer in zirconium, titanium and oxygen and has less aluminum than the neighboring zones (Figure 6b). The high-energy

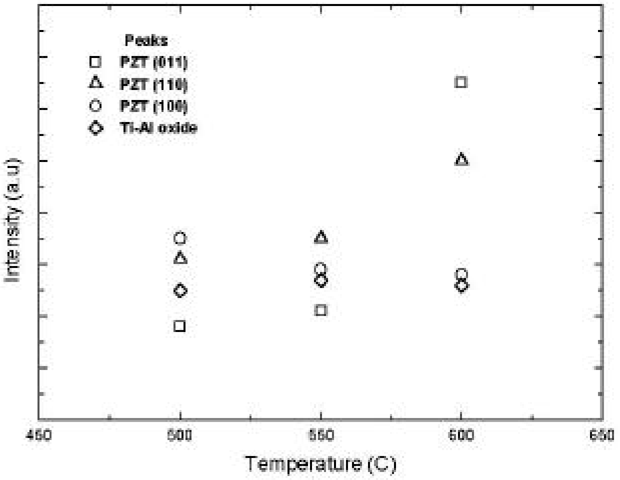

Figure 3. Peak intensity versus thermal treatment - deposition temperature of PZT film on Si substrates.

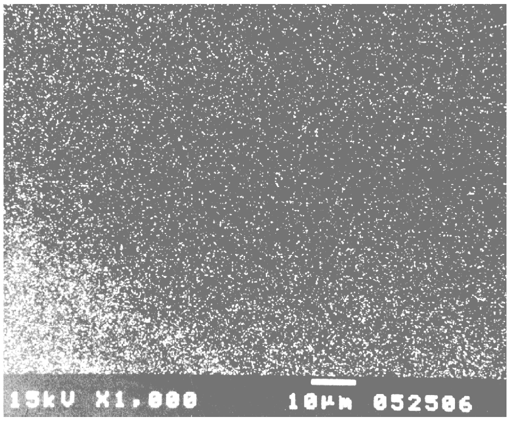

Figure 4. SEM image of the surface of PZT thin film.

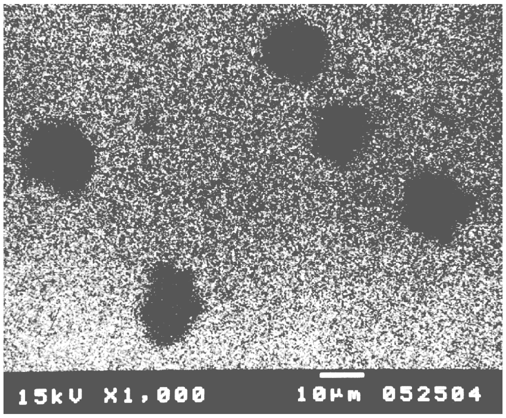

Figure 5. An example of circular zones on PZT thin film observed by SEM.

part of EDS spectrum over these circular zones (Figure 6a) reveals that they contains less lead and titanium than the neighboring zones (Figure 6b).

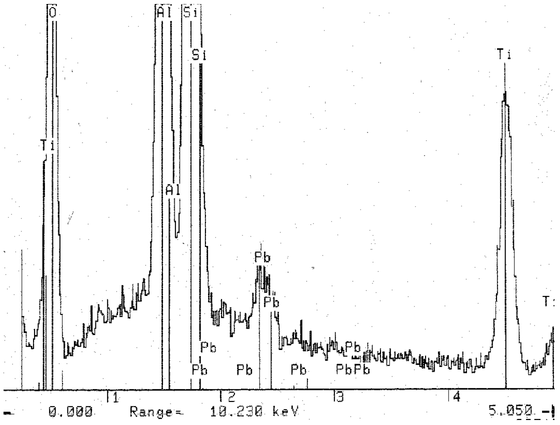

Figure 6a. EDS spectra of a circular zone on PZT film

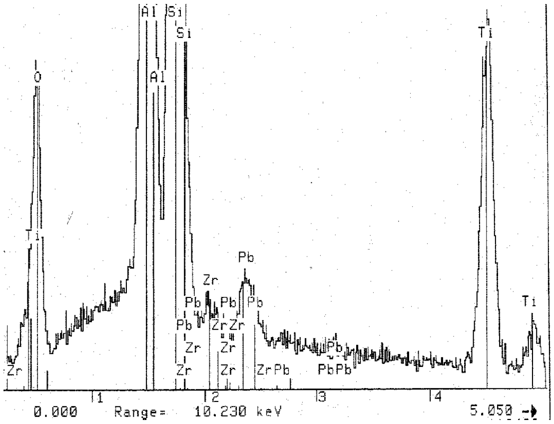

Figure 6b. EDS spectra outside of a circular zone
on PZT film.

Two possible explanations are proposed for the presence of these regions. One is that Ti-Al layer defects are generated during the annealing and deposition process; these defects affect the film growth producing the irregular chemical element incorporation.The second reason could be related to ferroelectric domain phenomena. Although the diameter of the circular zones is too large, a previous report on PZT films prepared by sputtering and sol-gel using SEM for surface characterization associated similar zones of a reduced diameter to a domain structure [12]. Currently ferroelectric domains observations by SEM is carried out at low accelerating voltages and in this work we have used voltages as high as 15kV thus we could be charging or altering the domains structure but domains still would be visible. More analyses are necessary to successfully explain these observations.

4. Conclusions

In conclusion by using a high oxygen pressure RF sputtering technique we have obtained PZT films on oxidized (111) silicon substrates. The quality of PZT films is improved if a previous annealing process is applied to the substrates as determined by XRD, SEM and EDS. This is specially noticeable when the annealing temperature and deposition temperature are 600°C. Electron microscopy and electron microprobe analysis revealed the presence of circular zones on the films surfaces whose origin could be related to a mixture of phases or to a ferroelectric domain structure. However, more work is needed to clarify these phenomena. Dielectric characterizations as well as high-resolution electron microscopy and SEM observations under low accelerating voltages are in progress and the results will be published separately.

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