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$PbTiO_3$ thin films grown by mixed reactive thermal co-evaporation

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Abstract

This paper describes the growth conditions and the structural characterization of thin films $PbTiO_3$ elaborated by a mixed reactive thermal co-evaporation. In a same chamber, in oxygen atmosphere, the titanium source is deposited by electron beam evaporation of TiO_2 and the lead source is brought by thermal evaporation of PbO. Crystallographic properties are presented using X-ray diffractometry, morphological aspects are shown by means of electronic and atomic force microscopes (MEB and AFM). The effect of post-annealing on morphology is presented.

Keywords: A1. Characterization; A3. Physical vapor deposition process; B1. Titanium compounds, $PbTiO_3$; B2. Ferroelectrics

1. Introduction

Recently, $PbTiO_3$, PZT and PLZT thin films have been largely studied. These ferroelectric materials have a wide number of possible applications such as optoelectronic devices, non-volatile memories [1–4] and pyroelectric devices [5]. Thin films of high quality are required to obtain powerful devices.

Lot of techniques have been employed for thin films elaboration. Usually, $PbTiO_3$ were deposited by sputtering method [6], pulsed laser deposition [7], sol–gel [8,9], metal-organic chemical vapor deposition [10,11], reactive molecular beam epitaxy [12] and reactive electron beam co-evaporation [13].

In this paper, we have chosen to deposit $PbTiO_3$ by using mixed thermal reactive methods: in a same chamber under oxygen atmosphere, the titanium source is deposited by electron beam evaporation of TiO_2 and the lead source is brought by thermal evaporation of PbO. We have used these materials to promote oxidation of deposited films. The growth method is first described, and then the results of films characterizations are exposed. Crystallographic properties are presented using X-ray diffractometry, morphological aspects are shown by means of electronic and atomic force microscopes (MEB and AFM). The effect of post-annealing on morphology is presented.

2. Experimental details

Fig. 1 shows the synoptic scheme of the deposition chamber [14,15]. Sources, which are made of PbO powder and TiO_2 pellets, were, respectively, positioned in a furnace and in an electron beam gun crucible. The substrates are $10\,mm \times 10\,mm$ oxidized silicon squares ($2\,\mu m$ thick SiO_2 on (1 0 0) Si). Height substrates are fastened on a heater furnace at equal distance directly above the two evaporating hearths. A residual pressure of 2×10^{-6} Torr is achieved using a Balzers TCP $500\,l \times s^{-1}$ turbomolecular vacuum unit associated with LN_2 cooled baffle. The gas composition was monitored by a quadripole mass spectrometer Balzers QMG 311. A metal foil covered the borders of each substrate to provide a sharp edge on the film for metric thickness measurement.

The growth conditions are reported in Table 1. The substrates are heated to 400 °C, the electron beam gun voltage was 5 kV for TiO_2, the oxygen partial pressure is held to 7×10^{-5} Torr. The rates of evaporation were controlled by two independent quartz monitors. The films thickness is measured *in situ* by quartz crystal oscillators

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and confirmed by Talystep profilometer. The films composition was calculated from growth rates taking into account the distances crucible-furnace and sample-quartz. The crystalline phases were deduced from X-ray diffraction (XRD) diagram. After deposition, the layers were annealed in Rapid Thermal Annealing Jetfirst 100 under oxygen at 550 °C. The effect of post-annealing as function of heating time is studied.

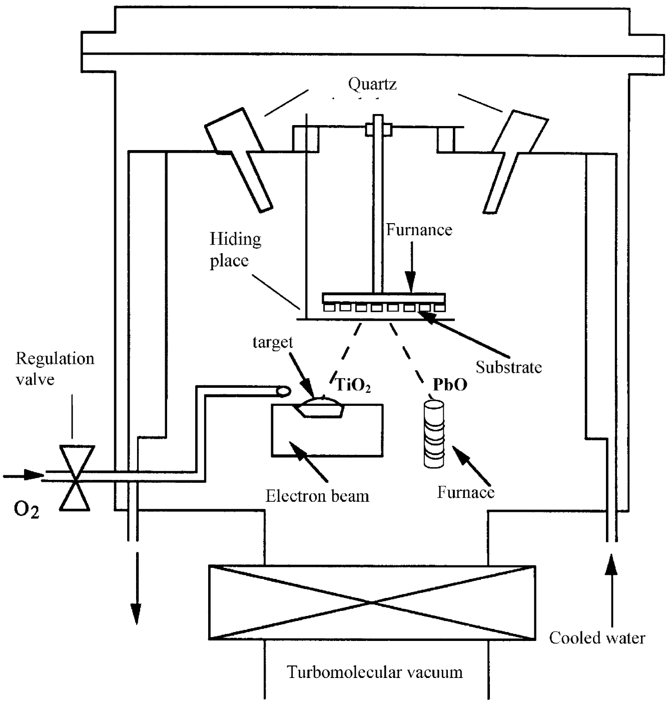

Fig. 1. Schematic diagram of the mixed thermal reactive co-evaporation system.

Table 1
Growth conditions of $PbTiO_3$ elaborated by the mixed thermal co-evaporation of TiO_2 and PbO

Mixed thermal co-evaporation	TiO_2	PbO
Substrate temperature	400 °C	
Residual pressure	2×10^{-6} Torr	
Reactive gas	O_2	
Partial pressure	7×10^{-5} Torr	
Electron beam gun voltage	5 kV	—
Current of electron beam filament	30 A	—
Current in heating furnace	–	5 A
Growth rate	≈1.6 Å/s	≈2 Å/s
Film thickness	0.4 μm × 1.2 μm	

The films concentration depend largely on geometry of the hearths. We observed a gradient concentration along the substrate holder as function of the position of the samples. The distribution of TiO_2 concentration is shown in Fig. 2. We obtained a high concentration of TiO_2 for the samples on the left part of the substrate holder (numbers 1 and 2), a high concentration of PbO on the right side (positions 7 and 8). The cones of evaporation are different

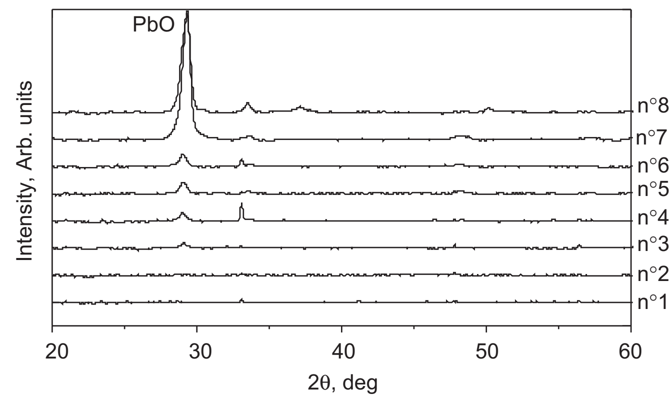

Fig. 3. XRD patterns of 1.2 μm $PbTiO_3$ phases according to site on the substrate holder before annealing.

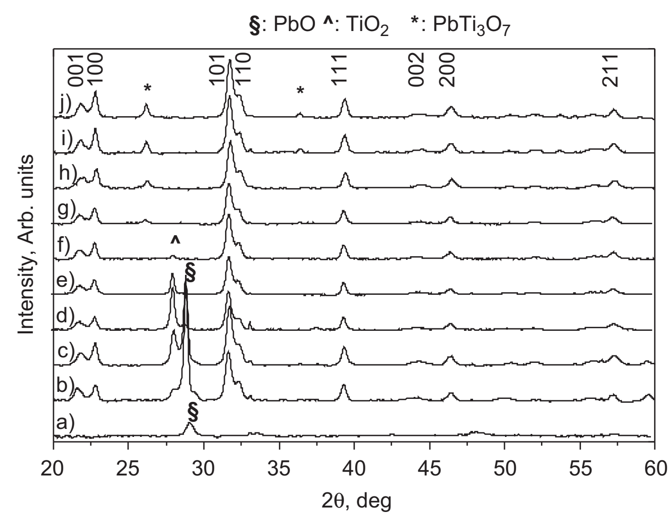

Fig. 4. Evolution of X-ray patterns of $PbTiO_3$ as function of annealing time at 550 °C for sample number 5: (a) 0 s, (b) 30 s, (c) 120 s, (d) 210 s, (e) 330 s, (f) 430 s, (g) 510 s, (h) 660 s, (i) 990 s, (j) 1320 s.

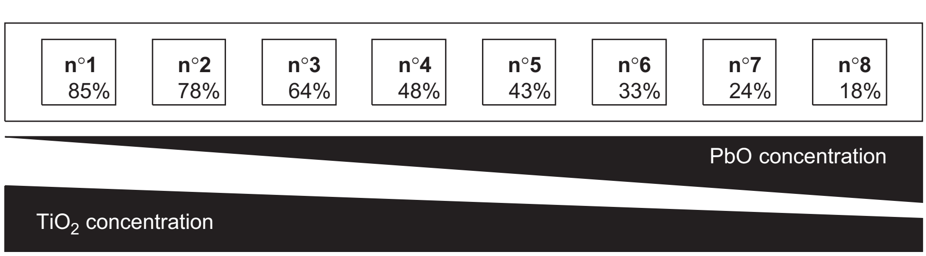

Fig. 2. Distribution of TiO_2 and PbO concentration along the substrate holder.