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Ferroelectric PbTiO₃ films grown by pulsed liquid injection metalorganic chemical vapour deposition

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Abstract: The influence of various deposition conditions (deposition temperature, partial oxygen pressure and solution composition) to the growth of ferroelectric PbTiO₃ (PTO) films by pulsed liquid injection metalorganic chemical vapour deposition (MOCVD) was examined. Films were grown on LaAlO₃ (001), SrTiO₃ (001) and sapphire (R-plane) substrates. Pb(thd)₂ and Ti(OⁱPr)₂(thd)₂ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) dissolved in toluene were used as precursors. The evolution of film composition, surface morphology and microstructure with deposition conditions was studied. The film microstructure was characterized by X-ray diffraction (XRD) in Bragg-Brentano and Schulz geometries and by Raman spectroscopy. Epitaxial films on perovskite substrates consisted of dominant c-axis and minor a-axis textured zones (*c*-domains and *a*-domains). The amount of *a*-domains in films depended mainly on deposition temperature. The twinning in *a*- and *c*-domains was observed and twinning (tilt) angles depended on deposition conditions and substrate. Fully twinned or partially twinned films were obtained in varying deposition conditions. The best quality epitaxial films were obtained on SrTiO₃ and LaAlO₃ at 650 °C. Films on sapphire were mainly polycrystalline.

Keywords: liquid injection MOCVD, PbTiO₃ films, twinning.

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1. Introduction

Lead-based ferroelectric oxides, such as PbTiO_3 (PTO), $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ (PZT) and etc., have been widely investigated as materials for applications in microelectronics [1], piezoelectric devices [2] and infrared sensors [3]. PbTiO_3 thin films attracted much attention due to high Curie temperature, low dielectric constant and high pyroelectric coefficient. Ferroelectric properties originate from the structural anisotropy, so high quality epitaxial films are required to take full advantage of the material properties and for applications in devices. Epitaxial PTO films have been grown by metalorganic chemical vapour deposition (MOCVD) [4-8], pulsed laser deposition (PLD) [9,10] and rf-magnetron sputtering [11]. Among various preparation methods, MOCVD has been recognized as the most promising technique due to the possibility to grow films on large area with high growth rate and good conformal step coverage.

In the literature, mainly liquid PbEt_4 and $\text{Ti}(\text{O}^i\text{Pr})_4$ compounds were used as precursors for MOCVD growth of PTO films by bubbling of carrier gas through containers of liquid precursors [5, 6, 12-16]. However, some other pairs of Pb and Ti precursors have been also studied: $\text{Pb}(\text{thd})_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) and $\text{Ti}(\text{O}^i\text{Pr})_4$ [17-20], $(\text{C}_2\text{H}_5)_3\text{PbOCH}_2\text{C}(\text{CH}_3)_3$ and $\text{Ti}(\text{O}^i\text{Pr})_4$ [21], $\text{Pb}(\text{OAc})_2$ and $\text{Ti}(\text{OnBu})_4$ [22], PbEt_4 and Ti-n-propoxyde [23] or PbEt_4 and TiCl_4 [24]. Only several works [25, 26] can be found on the use of solid $\text{Pb}(\text{thd})_2$ and $\text{Ti}(\text{O}^i\text{Pr})_2(\text{thd})_2$ or $\text{TiO}(\text{thd})_2$ precursors for PTO depositions. In these works, the vapour phase was generated by flash evaporation of a mixture of solid Pb and Ti precursors supplied into an evaporator. Solid metalorganic precursors are often preferred because they are non-toxic and more stable at room temperature as compared with liquid and extremely toxic tetraethyl lead precursor. In the last years, single source liquid injection MOCVD techniques have been more and more used for the growth of multi-component oxide layers. Moreover, these techniques allow an easier control of the composition of multi-component films and a better reproducibility of the process than conventional CVD.

In the present paper, we report on the role of oxygen partial pressure, deposition temperature and solution composition in the growth of PbTiO_3 films by pulsed liquid injection MOCVD using $\text{Pb}(\text{thd})_2$ and $\text{Ti}(\text{O}^i\text{Pr})_2(\text{thd})_2$ precursors dissolved in an organic solvent. The influence of such parameters on films microstructure, composition and morphology was studied.

2. Experimental details

Depositions were carried out by pulsed liquid injection MOCVD technique [27-29] in a vertical hot wall reactor. Microdoses (a few microliters) of an organic solution containing a mixture of metalorganic precursors were repeatedly injected into a hot evaporator using a special computer controlled injector. The vapour mixture (precursor + solvent) formed after flash evaporation of micro-doses was transported by an Ar+O₂ gas flow into a reaction chamber to a hot substrate. The main advantages of this technique are an easy control of precursor feeding rate, vapour and film composition. Moreover, precise and reproducible pulsed micro-dosing of precursor solution ensures growth like “digital”, and consequently a simple control of film thickness by pulse number.

Main deposition conditions are summarised in Table 1.

Pb(thd)₂ and Ti(thd)₂(OiPr)₂ precursors were synthesized and purified in our laboratory at Vilnius university. It is worth noting that the quality of precursors, especially of Pb(thd)₂, is crucial for obtaining good quality PTO films. For example, we tried to test some commercial Pb(thd)₂ precursors and we always had problems to prepare clear solutions without turbidity.

The morphology of the film surface was examined by using scanning electron microscopy (SEM) (Philips XL30) and atomic force microscopy (AFM) (Digital instruments Multimode Scanning Probe Microscope, tapping mode). Films on Si were etched with concentrated HF in order to form a step for thickness determination by profilometry. The film thickness on other substrates was measured from the film cross-section images obtained by SEM. Energy dispersive X-ray spectroscopy (EDS) or wavelength dispersive X-ray spectroscopy (WDS) analysis was used for the evaluation of the film composition. Crystallization, phase purity, in-plane and out-of plane orientation of the films were studied by X-ray diffraction (XRD) in Bragg-Brentano and Schulz geometries using a SIEMENS D5000 diffractometer with monochromatic CuK_{α1} radiation ($\lambda = 0.15406$ nm). The percentage of a-axis oriented domains (*A*, %) in the films was calculated by peak integration of the (102) reflection in φ -scans corresponding to the different domains:

$$A = \frac{2 * (I(102)_{\chi=58} + I(102)_{\chi=62})}{2 * (I(102)_{\chi=58} + I(102)_{\chi=62}) + I(102)_{\chi=27}} * 100\%,$$

where *I* is the peak integral intensity in φ -scans measured at different χ angles, corresponding to a-axis ($\chi=58^\circ$ or 62°) and c-axis ($\chi=27^\circ$) oriented crystallites (i.e. *a*- and *c*-domains). χ angles were determined from χ -scans of (102) reflection.

Raman spectra were collected using a Jobin-Yvon/Horiba Labram multichannel

spectrometer equipped with a liquid N₂ cooled CCD detector. Experiments were conducted in the micro-Raman mode at room temperature, in a backscattering geometry. The 514.5 nm line of an Ar⁺ laser was focused to a spot size smaller than 1 μm. The recorded spectra were calibrated using Si spectra at room temperature. The integration times were adjusted in order to have a high signal-to-noise ratio.

3. Results and discussion

3.1. Effects of oxygen partial pressure

In order to test the oxygen effect on Pb content of the film, PTO films were grown at 650°C at four different oxygen partial pressures. Composition analysis showed that the maximum Pb content in films was obtained using 37.5 % oxygen in the gas flow (Fig. 1a). The maximum growth rate (1.03 μm/h) of the films was obtained also at 37.5 % O₂. L.S. Hong et al. [13] established that an increase of O₂ concentration in gas promotes the PbO formation resulting in higher growth rate. However, too high oxygen concentration resulted in Pb deficient films, that was explained by stabilisation of high valency Pb₃O₄ and PbO₂ at higher O₂ partial pressures [13]. The optimum percentage of oxygen in the gas flow is highly dependent on the precursor type and its thermal stability. For example, in case of Pb(C₂H₅)₄ only 1 % of O₂ in gas flow was sufficient [13], while in our case it was necessary to use much more oxygen. In further depositions, we used 37.5 % oxygen in the gas flow.

Pb may be lost from PTO film during post-deposition treatment at higher temperatures or during the slow cooling after deposition at high deposition temperature. To get more information about the lead loss at high temperatures, several series of rapid thermal annealing (RTA) for 10 min at different temperatures and oxygen partial pressures were carried out. The composition of annealed films was analyzed by WDS and results are given in Fig. 1b. The films started to lose Pb at 700 °C and the Pb loss rate rapidly increased with further increase of annealing temperature. The lead content did not change after annealing at lower temperatures. One can see in Fig. 1b that the Pb desorption rate can be reduced by increasing oxygen partial pressure. It means that high oxygen pressure during cooling stabilizes the PbTiO₃ phase in our films. In order to minimize the Pb loss, we used 0.4 atm O₂ pressure during film cooling from high deposition temperature.

3.2. Composition and morphology

Series of films were deposited at different temperatures in varying the solution composition. The composition of films deposited on LaAlO_3 (LAO) was analyzed by WDS. Results are given in Fig. 2. It is evident that higher deposition temperatures require higher Pb precursor content in solution to achieve the right cationic proportion in the film. This may be related to higher lead oxide desorption at higher temperatures. At low $T_{\text{dep}} = 550^\circ\text{C}$, the Pb content in film gradually increases with the Pb content in solution. At higher deposition temperatures, the Pb fraction in the film increases until near stoichiometric value; it remains almost stable during further increase of the Pb content in solution. The minimum Pb content in solution necessary for achieving right Pb:Ti ratio in film may be named as “stoichiometric”. Although films grown from solution with Pb precursor excess may have right cationic ratio, they consist not only of tetragonal PbTiO_3 phase but also contain some additional phases ($\text{PbTi}_{0.8}\text{O}_{2.6}$, PbO).

The morphology of PTO films is very dependent on the solution composition especially for epitaxial films on LAO and SrTiO_3 (STO) substrates (Fig. 3). Films grown from Pb deficient or “stoichiometric” solutions on both substrates have similar surface morphologies. On the other hand, the morphology of PTO films on sapphire is fully determined by island growth at all deposition temperatures resulting in rather rough film surface ($R_a = 3\text{-}7\text{ nm}$).

Layers grown from solution with Pb deficit are made up of two zones, which become better separated in films deposited at higher temperatures (Fig. 3). XRD showed that these films consisted of tetragonal PTO and pyrochlore phases (Fig. 4). One zone is very smooth and the second one is formed from small crystallites. As these different zones are clearly visible by optic microscope, Raman spectra in each zone have been measured (Fig. 5). One can see that the smooth zone consists only of tetragonal PTO phase. The other zone presents a phase with lower symmetry than tetragonal PTO - it can be considered as monoclinic pyrochlore phase. Such film morphology (called “rosette-shaped”) was also observed by other authors [30-32] and was considered as perovskite islands in a pyrochlore matrix.

With the increase of Pb content in solution, smooth PTO zones become bigger and all the surface becomes smooth at $\text{Pb/Ti} = 1$ in the film. The morphology of PTO films is defined by two factors: island growth and twinning (this aspect will be discussed in detail in the next section). Twinning results in a film morphology with perpendicular line shaped zones [33]. At higher temperatures, twinning becomes the leading factor for surface morphology of PTO films. For example, the morphology of films grown at 650°C and higher temperature is mainly determined by twinning. Less twinned zones are observed in films grown at 600°C . The morphology of films deposited at 550°C is completely determined by island growth resulting

in a rather rough surface compared to the twinned layers. Thus, the roughness of the films grown from “stoichiometric” solutions decreases with the increase of deposition temperature (Fig. 6), and R_a reaches a very low value, 0.6 nm for films grown at 750 °C.

PTO films grown on STO substrates from solutions with Pb excess consist of spherical grains forming the structure of lines (Fig. 3). Such structure becomes more ordered with increasing growth temperature and at 700 °C the lines are quasi parallel. In contrast, films on LAO substrates consist also of spherical grains but the line shaped structure is not observed.

3.3. Microstructure

PTO films on sapphire are polycrystalline. XRD spectra of PTO films on LAO and STO substrates grown from “stoichiometric” solutions consist only of (00 l) and (h 00) reflections (Fig. 4a) corresponding to c -axis and a -axis textured crystallites, respectively (c - and a -domains). The best crystallinity was obtained for films deposited at 650 °C. PTO films on both STO and LAO substrates had very good in-plane orientation, as seen from pole figure for (102) reflection given in Fig. 7. Double peaks (split in χ angle) appear in pole figure of a -domains due to the domain twinning.

As it is known, a -domains and c -domains in epitaxial ferroelectric films are tilted by a small angle from the substrate plane normal due to the twinning phenomenon [4]. The a -domains and c -domains are bounded by the (101) twin plane, and this results in a tilt of [100] axis in a -domains, the tilt angle depending on the tetragonality of the cell (for $c/a = 1.065$ the tilt angle is 3.7 °) [4]. The tilt angle also depends on the domains volume fraction [34]. For films with a high fraction of c -domains, the c -domains tilt angle is very small [35]. Twinning is responsible for double rocking curves of (00 l) and (h 00) reflections and for the split in χ angle of peaks in pole figures (Fig. 7) of a -domains. Rocking curves of (001) reflection of PTO/LAO films deposited at different temperatures are given in Fig. 8. As mentioned about the surface morphology, twinning becomes a dominant factor when deposition is taken out at 650 °C or higher temperatures whereas the microstructure of layers deposited at lower temperatures is mainly determined by island growth. When layer is fully twinned (grown at temperatures ≥ 650 °C), the (001) rocking curve is double (Fig.8). The rocking curves of films deposited at lower temperatures are different. They become triple for film grown at 600 °C and lower temperatures: the peaks on both sides correspond to twinned zones and the central peak to non-twinned zones. This is in agreement with the fact that films grown at temperatures ≤ 600 °C are less or non-twinned and less textured than films obtained at higher temperatures. The twinning

angles (tilt angles) for a - and c -domains (α_a and α_c respectively) in PTO films grown at various temperatures were estimated from rocking curves of (001) and (100) reflections and are given in Fig. 9. PTO films on STO have a highly dominant c -axis texture, so no split of rocking curve of (001) reflection in c -domains was observed. It is possible that the tilt angle of c -domains is too small to be detected.

PTO films grown at various temperatures on STO and LAO substrates consisted of both a - and c -domains (Fig. 10). However, the c -domains growth is dominant for all range of deposition temperatures because the a -parameter of PTO cell matches better the parameter of substrate cell. The quantity of a -axis (A , %) textured crystallites in PTO films is clearly related to the deposition temperature and reaches the minimum in highly crystalline films grown at 650 °C. As a -domains form only due to twinning, C.S. Ganpule et al. [33] proposed a relation between the twinning angles of a - and c -domains and the a -domains fraction. This relation perfectly works for our PTO films on STO and LAO substrates: $\tan\alpha_c/\tan\alpha_a$ linearly depends on $A/(1-A)$ (Fig. 11). The bigger the amount of a -domains, the bigger the tilt angle of c -domains and the smaller the twinning angle of a -domains.

4. Conclusions

The influence of various deposition conditions (deposition temperature, partial oxygen pressure and solution composition) was examined for the growth of PbTiO_3 (PTO) films on various substrates by pulsed liquid injection MOCVD.

The oxygen partial pressure influences the Pb loss during the film growth and post deposition thermal treatments. The maximum $\text{Pb}/(\text{Pb}+\text{Ti})$ ratio in the film was obtained using 37.5 % O_2 in the gas flow during the deposition. The Pb loss during the cooling from high growth temperature can be reduced using high O_2 pressure (0.4 atm).

The evolution of film composition, microstructure and morphology with solution composition at different deposition temperatures was investigated. Higher deposition temperatures requires bigger amount of Pb precursor in solution for achieving of the right cationic proportion in the film. This may be related to higher Pb desorption at higher temperatures. The solution composition and growth temperature highly influence the film morphology and microstructure. Epitaxial films on perovskite substrates consist of dominant c -axis and minor a -axis textured zones (c -domains and a -domains). The surface morphology is mainly determined by island growth for films grown at temperatures ≤ 600 °C and by twinning phenomenon for films grown at temperatures ≥ 650 °C. Fully twinned or partially twinned films

can be obtained by varying deposition conditions. Twinning is observed in both a - and c -domains and twinning (tilt) angles depend on a -domains fraction. The best crystallinity and the lowest a -domains fraction were obtained in epitaxial films grown at 650 °C on LaAlO_3 (001) and SrTiO_3 (001) substrates.

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Figure captions

Fig. 1: Pb content in PTO/LAO films: (a) influence of oxygen percentage in gas flow during deposition, (b) influence of annealing temperature and oxygen partial pressure.

Fig. 2: Composition of PTO/LAO films in relation with solution composition.

Fig. 3: AFM images ($2 \times 2 \mu\text{m}^2$) of various compositions PTO/LAO and PTO/STO films deposited at different temperatures. The average roughness Ra and Pb/(Pb+Ti) ratio (% in film) are given on photos.

Fig. 4: XRD patterns of (a) stoichiometric and (b) Pb deficient PTO/LAO films grown at 650°C .

Fig. 5: Identification of two zones with different morphology in Pb deficient PTO/LAO film: (a) Raman spectra of two zones, (b) image of optic microscope and (c) AFM image.

Fig. 6: Average roughness (Ra) of PTO films versus deposition temperature (Pb/Ti~1).

Fig. 7: Pole figure of (102) reflection of PTO/LAO film grown at 650°C .

Fig. 8: Evolution of (001) rocking curves in *c*-domains of PTO/LAO films with deposition temperature.

Fig. 9: Evolution of twinning angles in *a*- and *c*-domains with deposition temperature.

Fig. 10: Evolution of *a*-domains percentage (A, %) in films with deposition temperature.

Fig. 11: Relation between twinning angle and *a*-domains fraction ($A/(1-A)$) in PTO films.

Tables

Table 1: Deposition conditions for PbTiO₃ layers by pulsed liquid injection MOCVD

Substrates	SrTiO ₃ (100), LaAlO ₃ (001- in a pseudo-cubic setting), sapphire (R-plane), Si (001)
Substrate temperature, °C	550 - 750
Evaporation temperature, °C	280
Transport gas	Ar + O ₂
Total gas flow rate, l/h	60
Oxygen fraction, %	7-50
Total pressure, Torr	5
Precursors	Pb(thd) ₂ , Ti(thd) ₂ (O ⁱ Pr) ₂
Solvent	Toluene
Solution concentration (total), mol/l	0.04
Injection frequency, Hz	2
Thickness, nm	100-300

Fig. 1

Fig. 2

	$T_{\text{dep}} = 550\text{ }^{\circ}\text{C}$	600 $^{\circ}\text{C}$	650 $^{\circ}\text{C}$	700 $^{\circ}\text{C}$	
Lack of Pb	27.9 % 4.0 nm	40.1 % 3.3 nm	44.5 % 6.9 nm	36.3 % 9.3 nm	PTO/LAO
Pb/Ti = 1	47.9 % 1.0 nm	47.8 % 2.1 nm	48.1 % 0.8 nm	48.5 % 0.9 nm
Pb excess in solution	69.3 % 3.1 nm	47.9 % 3.3 nm	48.1 % 1.5 nm	48.0 % 1.7 nm
Pb excess in solution	30.2 nm	13.2 nm	2.1 nm	2.1 nm	PTO/STO

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11