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Microstructure and local electrical investigation of lead-free α-La_2WO_6 ferroelectric thin films by piezoresponse force microscopy

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ABSTRACT

La_2WO_6 (LWO) thin films with the α high-temperature orthorhombic polymorph have been grown on (001)-$LaAlO_3$ (LAO) substrates by pulsed laser deposition. The X-ray diffraction study evidences that the films are (00l)-oriented. This matching appears to be in good agreement with the compatibility between the α-LWO bulk/LAO substrate crystal lattices. Pole figure measurements lead to the following crystallographic relationships between the film and substrate: $[100]_{\alpha\text{-LWO}} \parallel [110]_{LAO}$, $[010]_{\alpha\text{-LWO}} \parallel [1\bar{1}0]_{LAO}$ and $[001]_{\alpha\text{-LWO}} \parallel [001]_{LAO}$. Film cell parameters measured on a $LaNiO_3$ buffer layer, setting as electrode for electric measurements, lead to $a = 16.217(5)$ Å, $b = 5.607(1)$ Å and $c = 8.918(8)$ Å. A Williamson–Hall plot carried out on a LWO film reveals that the microstrain is 0.16% along the growth direction while the coherent domain dimension is 16 nm. Piezoresponse force microscopy imaging and piezoloops recording demonstrate that these films are piezoelectric/ferroelectric on nanoscale.

1. Introduction

Ferroelectric thin films based devices attract many attention due to their industrial and commercial applications as sonar and ultra-sonic transducers, capacitors, Ferroelectric Random Access Memories, Micro and Nano Electromechanical Systems, nanogenerators and many other high technology devices [1]. The films which lead to the best ferroelectric/piezoelectric performances commonly contain lead as $Pb(Zr,Ti)O_3$ [2,3], $(Pb,La)(Zr,Ti)O_3$ [4] or $xPb(MgNb)O_3$-$(1-x)PbTiO_3$ [5]. However, in ecology and environment concerns, lead should to be replaced by less toxic elements [6]. Since the last 10–15 years, many works have been devoted in the development of lead-free ferroelectric materials in thin films. In this objective, compounds with attractive performances in bulk have been deposited in thin films while their ferroelectric properties have been investigated. This is especially the case for $BaTiO_3$ (BT) [7,8], $BiFeO_3$ (BFO) [9,10], $Na_{0.5}Bi_{0.5}TiO_3$ [11,12] and $K_{0.5}Na_{0.5}NbO_3$ [13]. For BT and BFO thin films, remnant polarizations (P_r) as high as ≈70 μC cm^{-2} and ≈100 μC cm^{-2}, respectively, were measured at room temperature [7,9]. For BT grown on (110)-oriented $DyScO_3$ substrate by Pulsed Laser Deposition (PLD), a noticeably enhancement of ferroelectricity was revealed, the P_r value being almost 270% of the 26 μC/cm^2 of single crystal BTO [14]. Such a phenomenon was explained in terms of lattice-strains induced by the substrate in the film. In fact, such a strain engineering was also consider to induce polar states/ferroelectricity in various other systems. We can point out the emergence of polar phase in $SrMnO_3$ films grown on (001)-oriented $(LAO)_{0.3}(Sr_2AlTaO_6)_{0.7}$ substrates by PLD [15], the evidence of room-temperature ferroelectricity in strained epitaxial STO films grown on (110)-$DyScO_3$ substrates by reactive Molecular Beam Epitaxy (MBE) [16], the emergence of a strong ferroelectric ferromagnet in strained (001)-oriented $EuTiO_3$ films grown on (110)-oriented $DyScO_3$ substrates by reactive MBE [17] and the highlighting of ferroelectricity in frustrated pyrochlore structure $La_2Zr_2O_7$ thin films grown on (110)-oriented STO substrates by a sol–gel method coupled to a spin-coating technique [18]. In fact, such a strain engineering was already taken into account to stabilize metastable phases as the cubic perovskite $La_4BaCu_5O_{12+\delta}$ phase found on both (001)-oriented MgO and (001)-oriented LAO substrates [19] or the $CaCuO_2$ "infinite layer" structure obtained on (110)-oriented $NdGaO_3$ substrate by PLD in the field of superconductivity [20].

In this purpose, we are interesting in a lanthanum tungstate compound, La_2WO_6 (LWO), when grown in form of thin film by PLD on LAO substrate. In bulk, two polymorphic structures exist for LWO. The low temperature variety named β-LWO which crystallizes in the space group $P2_12_12_1$ (n°19) with cell parameters $a = 7.5196(1)$ Å, $b = 10.3476(1)$ Å, $c = 12.7944(2)$ Å [21]. The high temperature form, labelled α-LWO [22], which crystallizes in the space group $Pm2_1n$ (n°31) with quenched cell parameters $a = 16.5531(1)$ Å, $b = 5.52003(3)$ Å, $c = 8.88326(3)$ Å for powder; besides, this phase presents a close relation with Scheelite and $Lu_{0.8}Nd_{1.2}WO_6$ structures

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[23]. The powder phase transition takes place at 1440 °C and it is a first order phase transition consequently the high temperature form could be quenched.

In fact, the two stabilized polymorphs, α and β, crystallize in a non centro-symmetric space group, and thus can lead to potential interesting ferroelectric properties. First observations of local ferroelectricity were recently obtained for LWO films grown on (001)-STO substrates [24]. In this study, thin film cell parameters were deduced from Reciprocal Space Mapping: $a = 16.585(1)$ Å, $b = 5.717(2)$ Å, $c = 8.865(5)$ Å.

In this paper, in a first step, we present structural results obtained for LWO thin films grown on bare (100)-oriented LAO single-crystal substrates (Crystal GmbH, Germany; $a_{pseudo\text{-}cubic} = 3.79$ Å). Then, we highlight microstructure and local electrical measurements recorded by piezoresponse force microscopy (PFM) on LWO films grown on (100)-oriented LAO substrates covered with a metallic $LaNiO_3$ (LNO) bottom electrode.

2. Experimental section

2.1. Experimental section

A β-LWO ceramic pellet, 1 in. in diameter and 5 mm-thick, was used as a target for laser ablation. The ceramic was prepared by solid state reaction route method, mixing dried oxides La_2O_3 and WO_3 weighted in stoichiometric proportions. Twice, with an intermediate grinding, the mixture was heated at 1350 °C in air for one night. The resulting powder was then ground, pressed in the form of a disc using an uni-axial press, sintered up to 1450 °C for 12 h in air and slowly cooled down to room temperature. The X-ray diffraction pattern confirms the existence of the low temperature phase β-LWO for the target with no impurity [21]. LNO target was elaborated by co-precipitation method [25,26].

Depositions were carried out with a Compex Pro 102 KrF excimer laser ($\lambda = 248$ nm). The fluence was adjusted to 2 J/cm^2 and the deposition rate was 2 Hz. The target-substrate distance was adjusted to d = 4.5 cm. For PFM experiments, heterostructure was needed as LAO substrate is not conductive. Thus firstly, LNO thin film, used as bottom electrode, was deposited on (100)-oriented LAO substrate and then LWO film was grown. All substrates were first ultrasonically cleaned in ethanol for 5 min, and then dried. The pressure in the pulsed-laser chamber was lowered down to 10^{-4} Pa. Then, the substrate temperature for the 34 nm-thick LNO film growth was raised through a 10 °C/min step elevation to synthesis temperature: 750 °C. In the case of LWO film, the substrate temperature is 900 °C and the thickness, corresponding to 6000 laser-pulse shots, is 50 nm.

All the films were deposited under dynamic O_2 pressure (10^{-3} Pa for LNO and 10 Pa for LWO) and finally oxidized under static oxygen pressure (2×10^4 Pa) during cooling.

The powder X-ray diffractograms were obtained on a Rigaku Ultima IV equipped with a Cu-anode X-ray ($\lambda_{K\alpha1} = 1.54056$ Å, $\lambda_{K\alpha2} = 1.54443$ Å).

The thin films crystalline nature (indexation, crystalline quality and pole figures) were characterized using a Rigaku SmartLab X-ray diffractometer equipped with a 9 kW rotating anode X-ray generator ($\lambda_{K\alpha1} = 1.54059$ Å). For Ω/2θ and rocking curves analysis, a high resolution configuration was used: the X-Ray beam was made parallel with a cross-beam optics and monochromatized with a double Ge (220) monochromator. In this study all the (Ω-2θ) scans were performed in the range of 10–80°, with a step size of 0.02° and a 1°/min speed. Pole figure measurements were made in a medium resolution configuration coupled with an in plane geometry.

The surface topography and nanoscale piezo −/ferroelectric properties of the films were studied using atomic force microscope (AFM) (MFP-3D Asylum Research) working in contact mode under environmental conditions. Switching behaviour and piezo-activity for ferroelectric domains were probed by PFM imaging and by recording local hysteresis piezoloops. Pt/Ir conductive tips coating (nanosensors PPP-NCHPt probes, $k \sim 3$ N m^{-1}) and ground conductive substrates were used to perform these experiments. Detailed information can be found elsewhere [27,28].

3. Crystalline structure

A first part of the crystalline structure will be dedicated to the LWO deposition on (100)-oriented LAO. The second part will present the addition of a LNO buffer layer between LAO and LWO acting as bottom electrode.

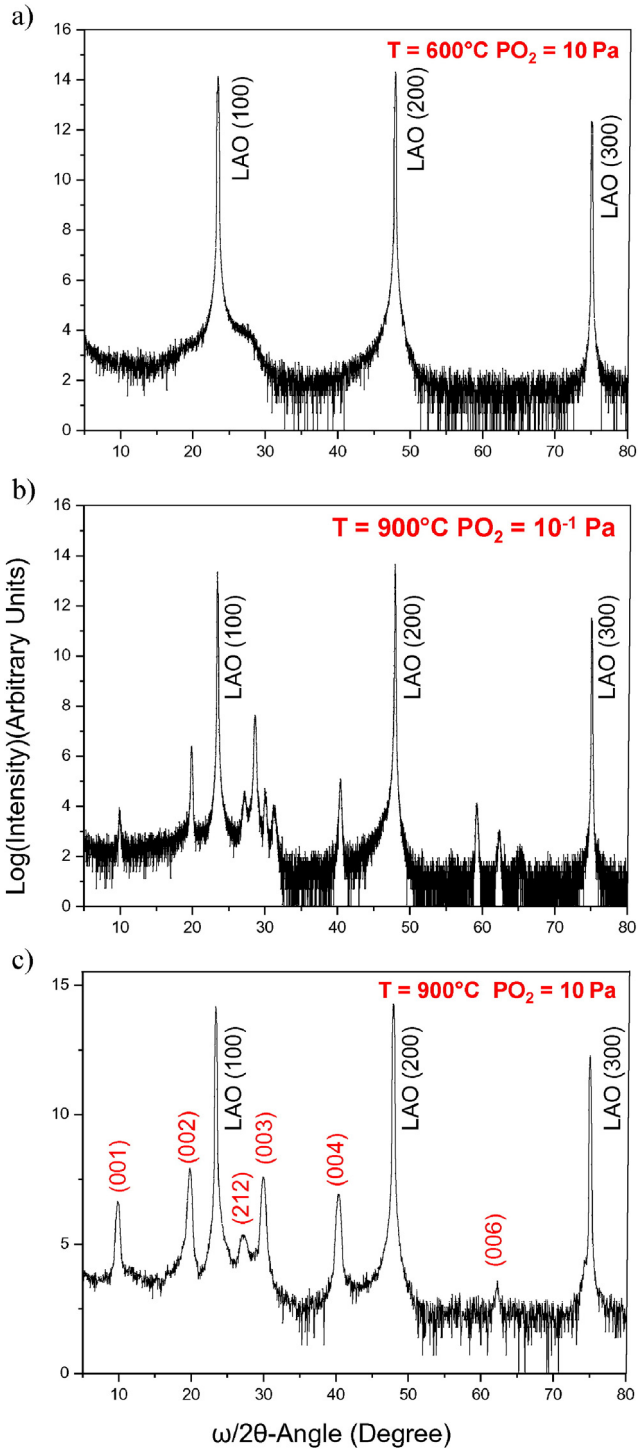

Fig. 1. X ray diffractograms of α-LWO thin film deposited on (001)-LAO. a) T = 600 °C and $PO_2 = 10$ Pa; b) T = 900 °C and $PO_2 = 10^{-1}$ Pa; c) T = 900 °C and $PO_2 = 10$ Pa.

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