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A: Regular paper

Lead potassium niobate thin films grown by Pulsed Laser Deposition

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Abstract: By pulsed laser deposition, lead potassium niobate $Pb_2KNb_5O_{15}$ was grown on (001) oriented $Gd_3Ga_5O_{12}$ substrate using a platinum buffer layer. The PKN thin films were characterized by X-Ray diffraction and Scanning Electron Microscopy (SEM). The dependence of their structural properties as a function of the deposition parameters was studied. It has been found that the out of plane orientation of PKN film depends on the oxygen pressure used during the growth. Indeed, PKN thin film is oriented [001] for low pressure and is oriented [530] for high pressure. For these two orientations, the crystalline quality of PKN film was determined using omega scans.

Keywords: Ferroelectric thin film, TTB-structure, PLD, PKN

Introduction

In the recent years, some studies have shown the increasing interest of materials with tetragonal tungsten bronze (TTB) structure by demonstrating their potential technological applications [1–5].

Among the tetragonal tungsten bronze (TTB) oxides, lead potassium niobate $Pb_2KNb_5O_{15}$ (PKN) is one of the best-known compounds [6,7]. It has an orthorhombic structure at room temperature with cell parameters: a=17.754(2) Å, b = 18.014(2) Å and c = 3.915(1) Å [8]. PKN ceramic presents a behavior of a classical ferroelectric and undergoes a ferroelectric-paraelectric phase transition at Tc=450 °C [9], changing the point symmetry from P4/mbm (N° 127, paraelectric) to Cm2m (N° 38, ferroelectric). At room temperature PKN is ferroelectric and ferroelastic as refined by Sciau et al. [7]. The ferroelectric polarization in PKN is oriented along the b axis of the orthorhombic unit cell. Above Curie temperature, PKN is paraelectric and paraelastic with a tetragonal symmetry (space group *P*4/*mbm* N° 127) [9].

PKN was previously studied for its piezoelectric, ferroelectric-ferroelastic coupling, optical properties, and surface-acoustic-wave (SAW) properties [6,9–13]. So PKN thin films can be of a great interest for ferroelectric and ferroelastic applications. Furthermore, the higher Curie temperature of PKN makes it very interesting for several optical and ferroelectric-ferroelastic coupling applications [10].

Because of the complexity of the TTB structure [14], compounds with such structure as thin films are very rare,

especially because, nowadays no TTB-structure substrates are available. In this context, realization of TTB-structured thin films is a significant issue. Herein, we make a proposition to grow oriented PKN thin film by choosing an adapted substrate.
Pulsed Laser Deposition (PLD) technique is also known and repeated to be adapted to grow usually complex structures since it uses a UV laser for a congruent transfer from target to substrate.

Experimental

PKN target was prepared by a solid state reaction starting from the oxides K_2CO_3, Nb_2O_5 and PbO (Sigma Aldrich, 99.99 %):

$$4PbO + K_2CO_3 + 5Nb_2O_5 \rightarrow Pb_4K_2Nb_{10}O_{30} + CO_2 \quad (1)$$

The Stoichiometric mixture was dried at 650 °C for 6 h, and then annealed at 1100 °C for 20 h. The obtained powders were pressed into ceramics of about 2cm in diameter and 5 mm in thickness. The TTB structure with orthorhombic cell (a=17.754(2) Å, b = 18.014(2) Å and c = 3.915(1) Å) was confirmed by using X-ray diffraction (XRD).

PKN thin film has been grown on (001)-$Gd_3Ga_5O_{12}$ (GGG) substrates by pulsed laser deposition. 50 nm thick Platinum (Pt) buffer layer was also deposited by pulsed laser deposition, this will serve as bottom electrode for further electrical measurements. The following table summarizes the PLD parameters used to grow PKN thin film:

Table 1: Experimental conditions used to grow PKN and Pt films by PLD

	Pt layer	PKN films
Substrate temperature	25 °C	750 °C
Oxygen pressure	10^{-6} mbar	0.03 and 0.15 mbar
Target-substrate distance	2.5 cm	3.8 cm
Laser frequency	5 Hz	3 Hz
Time deposition	13 minutes	55 minutes
Laser fluency	2.5 J/ cm^2	1.9 J/cm^2

Note that the temperature of 750 °C is the minimum necessary to achieve good crystallinity for PKN films. Indeed, below 750 °C no Bragg peak related to PKN phase was detected by XRD.

Two different values of oxygen background pressure were used to elaborate PKN thin films (0.03 and 0.3 mbar). After deposition, the average thickness of the obtained films, controlled by the deposition rate, was around 200 nm (±10%) for PKN and 50 nm for Pt. The deposition rate was determined from thick films using DEKTAK profilometer in PKN case, and from the simulation of Laue oscillations in the case of Pt layer (see results section).

The films were systematically characterized by X-ray diffractometry performed on a two-circle Siemens D5000 diffractometer using θ-2θ and rocking curves scans. All experiments were performed using a 0.1mm slight before and after the sample. The X-ray tube was operating at 40 kV and 40 mA (Kα Cu: 1.54056 Å). SEM micrographs were performed using FEI-Quanta 200F microscope.

Results and discussion

Gadolinium Gallium Garnet (GGG) [15] substrate is an oxide with cubic structure with $m3m$ symmetry, its bulk cell parameter is a=12.382 Å. It is usually used as substrate to grow epitaxial iron and yttrium garnet. Because of its cell parameter, which is so close to that of general TTB materials, GGG substrate can be of a great interest to grow oriented and epitaxial TTB compounds.

As shown in table 1, PKN thin film has been deposited under different oxygen pressures, 0.03 and 0.15 mbar. Fig 1 shows X-ray diffractogram of 200 nm thick PKN film grown on Pt(50nm)/GGG substrate. We note that Pt layer is oriented along its [111] direction. Smooth and well-structured Laue oscillations appeared from either side of the (111)Pt peak indicating a good crystalline quality of Pt layer along the growth axis. These oscillations have been simulated and allowed to control with precision the Pt layer thickness. Pt out of plane lattice parameter deduced from this diffractogram, assuming a cubic structure, is c_{Pt} = 3.924 Å (± 3%). The simulation was performed using the following relation:

$$I = I_o \frac{\sin^2(2\pi c N_c \sin\theta/\lambda)}{\sin^2(2\pi c \sin\theta/\lambda)} \quad (2)$$

Where: I is the diffracted intensity, c the lattice parameter and Nc the number of unit-cells along the growth axis.

Concerning PKN film, in the case of low pressure (0.03 mbar, fig 1 (a)), only the (00ℓ) Bragg reflections can be seen. PKN is oriented [001] and its polar axis is parallel to the substrate. The out-of-plane cell parameter deduced from this diffractogram is c_{PKN}=3.932 Å (± 1%). This value is higher than the c-cell parameter in bulk PKN (c=3.915 Å), which means that PKN should be strained in the plane by the substrate. In addition, we observe that the peak (002)PKN is narrower than the (111)Pt: remember that the peak width is inversely proportional to the crystallites size along the growth direction. Thus, PKN film crystallites size would be larger than that of the Pt layer.

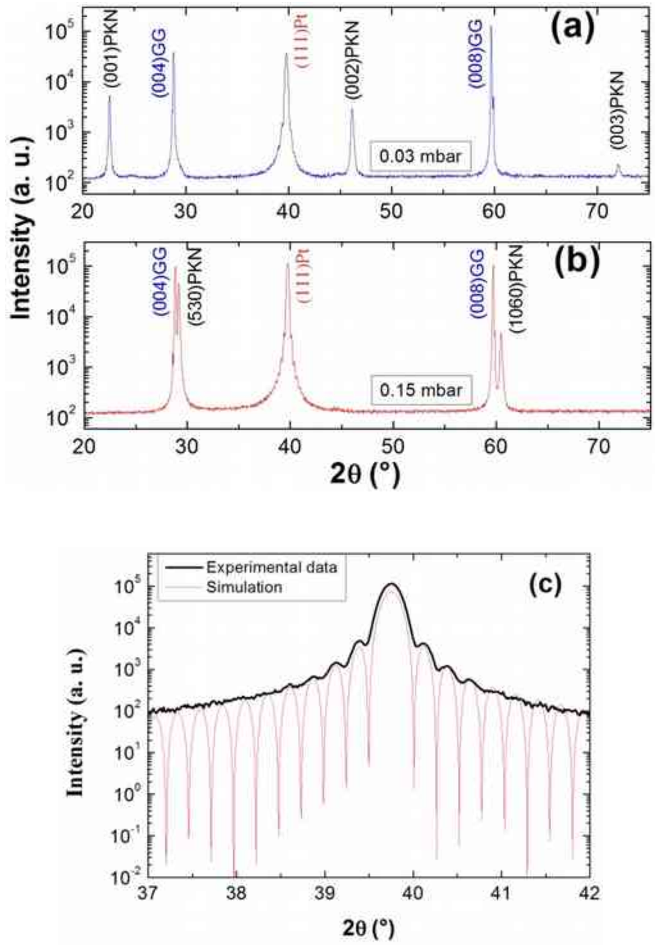

Figure 1: Semilogarithmic θ-2θ X-ray diffractograms of PKN thin film

Films are of about 200 nm in thickness, deposited on Pt(50 nm)/GGG substrate under oxygen partial pressures of a): 0.03mbar and b): 0.15 mbar. C): zoom around (111)Pt peak showing Laue oscillations fit.

In the case of high pressure (0.15 mbar, fig 1 (b)), besides (00ℓ)GGG and (111)Pt peaks, only the (530) and its upper order (10 60) Bragg reflections related to PKN are observed. In these conditions, PKN thin film is clearly oriented [530]. This result is very reproducible even for very low thicknesses. For this orientation, any PKN cell parameter cannot be deduced from this diffractogram. However, the polar axis of the orthorhombic cell is out of the substrate plane. This will be more suitable for some ferroelectric applications that requires out of plane polarization switching.

Films mosaicity was investigated by omega scans performed around the reflections of PKN, Pt and GGG substrate (Fig. 2). In the case of [001]PKN, the Full Width at Half Maximum (FWHM) of (111)Pt and (002)PKN are about three times as high as that measured on (004) GGG, which was 0.30°. Also, it is so important to note that the mosaicity in PKN film (1.3°) is quite comparable to that of the Pt layer. So, one can conclude that the mosaicity in PKN is mainly due to the Pt layer.

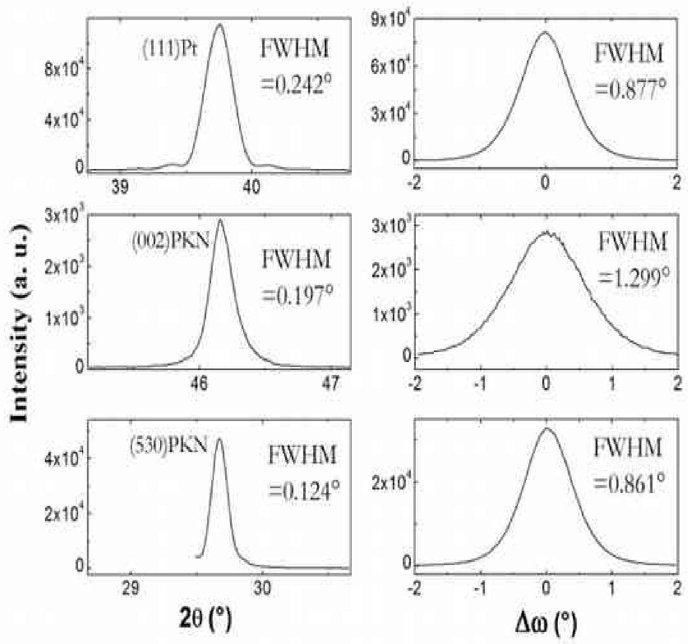

Figure 2: θ-2θ (left) and omega (right) scans performed around: (111)Pt, (002)PKN and (530)PKN respectively.

In the case of [530]PKN film, both Pt and PKN layers show a large mosaicity along the growth axis. Values are similar to that obtained for [001].

Moreover, omega scans show a smaller mosaicity compared to that in PKN oriented [530]. All values are summarized in the table 2.

Table 2: FWHM of Bragg peaks relative to the substrate and to the Pt and PKN films.

	Δ2θ (°)	**Δω (°)**
(004)GGG	0.044	0.310
(111)Pt	0.242	0.877
(002)PKN	0.197	1.299
(530)PKN	0.124	0.861

Fig. 3 shows SEM micrographs performed on the top surface of the PKN thin film. One can see regular surfaces with an homogeneous microstructure and uniform grain distribution. For the low pressure deposition film (i.e. (001)PKN thin film), the

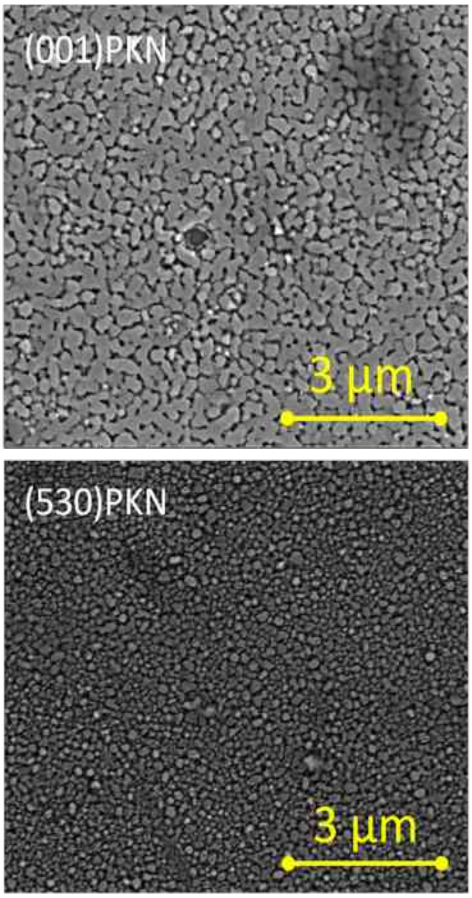

Figure 3: SEM pictures of the previously presented (001)PKN and (530)PKN thin films respectively.

grains are flat and parallel to the substrate surface. In contrast, for the high pressure film deposition (i.e. (530)PKN thin film) the grains have rather spherical shape. We also note that the average grain size is similar for both films, which is due to the used elaboration conditions (the same temperature, 750°C). The films surface doesn't present any cluster nor PLD droplets, due to the optimized laser energy.

Conclusion

Lead potassium niobate thin films have been successfully elaborated using pulsed laser deposition on (111)Pt/(001)GGG. PKN thin films orientation can be controlled by setting up the oxygen partial pressure during the growth. In fact, as function of the oxygen partial pressure, PKN grew with in-plane or out-of-plane ferroelectric polarization.

This study clearly demonstrated that the (111)Pt layer determines PKN orientation. This assumes that the growth of PKN on Pt/Si substrate would be quite possible; because the growth of platinum is already mastered on Si and (111)Pt/Si substrates are available. This makes PKN compound compatible with an implementation in microelectronic devices, especially because lead based TTB compounds, such as PKN, often show partial ferroelastic-ferroelectric coupling properties, which is very advantageous for memories and optical gates applications.

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