Pulsed Laser Deposition and Characterization of \( \text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3 \) Thin Films

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Abstract

Ferroelectrics are materials with a number of interesting properties for a wide range of applications. Many ceramics with good ferroelectric characteristics have been developed but most are based on lead, which is a toxic material and whose usage is now restricted in the EU. A strong candidate to replace these materials is \( \text{Na}_{x}\text{K}_{1-x}\text{NbO}_3 \) (NKN) which exhibits attractive piezo- and ferroelectric properties. Most of the research on this subject was conducted on bulk ceramic samples.

Thin films of \( \text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3 \) were grown on Pt/Si and sapphire substrates by Pulsed Laser Deposition. The effect of the deposition parameters was investigated. An ideal deposition pressure of 0.2 mbar for the present PLD system was determined and the temperature above which widespread crystallization begins was found to be in the 500ºC-530ºC range. Fully developed crystallites were observed with SEM for films grown at 600ºC. Film thicknesses of up to 500nm were obtained from ellipsometric spectra. Transmission, absorption and reflection measurements allowed the energy gap to be estimated, with values in the 3.4-3.9 eV range. EDS revealed that unwanted evaporation of Na and K took place, leaving an excess of Nb. C-f and R-f measurements showed the poorly resistive (leaky) nature of the films, with high values of loss tangent. We suggest that future work invests time on improving the stoichiometry of the films.

Keywords: PLD, NKN, Ferroelectrics, Lead-Free

1 Introduction

Ferroelectrics are materials with a number of interesting properties that make them very sought after for a wide range of applications by scientific community and industry alike. \( \text{BaTiO}_3 \), BST, PZT, PLZT, PMN and more recently PST are some of the most successful ferroelectric ceramics and deserved the attention of scientists in the last decades. However, despite their attractive ferroelectric properties these materials (especially the ones based on lead) have a hazardous impact on the environment and their usage has become increasingly restricted by legislation such as EU’s 2006 WEEE and RoHS initiatives.
Additionally, the recent trend in medical investigation of looking for ways to incorporate in human beings devices that can help monitor bodily functions has led to renewed interest in ferroelectric materials and, due to their toxicity, the usage of this kind of ceramic is not acceptable. Among the lead-free materials that have been suggested as replacement are the ones that belong to a family represented by the chemical formula Na$_x$K$_{1-x}$NbO$_3$ also known as NKN.

Various techniques have been employed to prepare NKN thin films. Pulsed Laser Deposition (PLD), is commonly used due to its versatility, ease of use, cost effectiveness and ability to grow films with stoichiometric ratios very similar to those of the targets that originated them.

This thesis focuses on NKN thin films and their preparation by PLD and investigates the effects of deposition parameters on the structure, morphology, and composition of these films. The chosen NKN target was Na$_{0.5}$K$_{0.5}$NbO$_3$. A variety of characterization techniques were employed, among which SEM, AFM, XRD, EDS and Ellipsometry. Optical transmission, reflection and absorption were also studied. Finally, characterization of electrical properties of the films was attempted.

2 Ferroelectric Materials

The Piezoelectric effect

A ferroelectric materials is, before anything else, a piezoelectric, which is to say that a the charge density $D$ of a material is linearly dependent on an applied stress $T$ (direct piezoelectric effect) and, in turn, the strain $S$ shows a linear dependency on the applied electric field, $E$ (converse piezoelectric effect). Mathematically, we have [1]:

$$ [D] = [d][T] + [\varepsilon][E] $$  \hspace{1cm} (direct)  \hspace{1cm} 2.1.

$$ [S] = [s^T][T] + [d]^T[E] $$  \hspace{1cm} (converse)  \hspace{1cm} 2.2.

Where $[\varepsilon]^T$ is the matrix of dielectric permittivity, $[s^T]$ the matrix of material compliance and $[d]$ is the matrix of piezoelectric coefficients.

Of the 32 crystal point groups, all but the 11 centrosymmetric groups and the point group 432 are capable of exhibiting the piezoelectric effect. Examples of piezoelectric materials include quartz, ZnO and PZT (Pb(Sr,Ti)O$_3$).[2]

The Pyroelectric effect

Ferroelectric materials are also pyroelectric, i.e., they exhibit a temperature dependent spontaneous polarization, $P_s$. Mathematically, this effect can be expressed as follows:

$$ p_i = \frac{\partial P_{s,i}}{\partial T} $$  \hspace{1cm} 2.3.

Where $p_i$ (Cm$^2$K$^{-1}$) is the vector of pyroelectric coefficients.

Pyroelectric materials belong to 10 polar crystallographic point groups which are a subset of noncentrosymmetric point groups. As such, pyroelectric materials are also piezoelectric. Apart from being piezoelectric, as mentioned above, ZnO and PZT are also pyroelectric materials [2].
The Curie point

Most ferroelectric materials undergo a phase transition from a high-temperature non-ferroelectric (paraelectric) to a low temperature ferroelectric phase which, invariably, has lower symmetry than the high temperature phase. The temperature at which this transition occurs is called the Curie point, \( T_C \). In most ferroelectrics, the temperature dependence of the dielectric constant above the Curie temperature can be described reasonably accurately by the Curie-Weiss law:

\[
\varepsilon = \varepsilon_0 + \frac{C}{T - T_0}, \quad T > T_0 \tag{2.4}
\]

where \( C \) is the Curie constant, \( T \) the temperature and \( T_0 \) is the Curie-Weiss temperature.

Ferroelectric thin films

The trend in recent years has been toward the development of thin films. The preparation of these layers with thicknesses typically between 100nm and 2 \( \mu \)m can offer many advantages, among which:

- Smaller size
- Less weight
- Easier integration of IC technology
- Lower operating voltage

3 Na\(_x\)K\(_{1-x}\)NbO\(_3\)

Summary of properties

NKN is a ferroelectric material with a perovskite structure, a rich phase diagram and good ferroelectric properties for a no-lead material.

Reported values for \( \varepsilon_r' \) range from as low as 38 [3] to as high as 520 [4]. The dielectric constant depends, however, on the temperature of the material and in the vicinity of \( T_C \) it can reach values as high as 5000 [20]. In the case of \( d_{33} \), typical values are in the 80-160 pC/N [5]. Coercive fields usually take values in the 2-4 kV/mm interval [6], even if coercive fields as high as 8.5kV/mm have been reported [7]. Values of \( P_r \) as low as 3.54\( \mu \)C/cm\(^2\) [8] and as high as 30.2\( \mu \)C/cm\(^2\) have been reported [6]. Cho and Grishin have measured remnant and spontaneous polarizations of 10\( \mu \)C/cm\(^2\) and 17.5\( \mu \)C/cm\(^2\), respectively [9]. The Curie temperature of NKN has been reported as being 400ºC [5].

Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is a thin film deposition technique where a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited. This material is vaporized from the target in a plasma plume generated due to photon interaction and which deposits it as a thin film on a substrate. This process can occur in ultra-high vacuum or in the presence of a background gas, such as oxygen. The main advantages in the usage of this technique are:

- Conceptual simplicity: a laser beam vaporizes a target surface, producing a film with the same composition as the target.
• Versatility: many materials can be deposited in a wide variety of gases over a broad range of gas pressures.
• Cost-effectiveness: one laser can serve many vacuum systems.
• Speed: high quality samples can be grown reliably in 10 or 15 minutes.
• Scalability: complex oxides move toward volume production.
• Stoichiometry: films grown with this technique usually follow the stoichiometric ratios of their targets closely

Articles describing PLD growth of NKN thin films include [9] [10] [11].

4 Experimental setup and procedure

The PLD system

The laser used for target ablation is an Nd:YAG based one, i.e., the lasing medium is an Nd:YAG (neodymium-doped yttrium aluminum garnet, Nd:Y_2Al_5O_{12}) crystal. This type of laser can emit radiation with wavelengths of 1064, 532 and 266 nm. For this experiment, the 266nm UV line has been selected. In this case the energy of the laser radiation is absorbed in the first layers of the target surface which reduce drastically the number of particles on the growing film surface.

Inside the cavity, the temperature of the substrate can be varied by applying a voltage across a filament of MoSi_2 protected by a tube of fused SiO_2 that is in close proximity to the substrate. The substrate is also connected to a multimeter that constantly reads the temperature of the substrate. Roughly 3 cm below the support where the substrate is placed, an hexagonal hole houses the target.

To generate vacuum inside the chamber, two pumps are connected to it. The first, a rotational pump is responsible for lowering the pressure to ~10^{-2} mbar. After this step, a turbomolecular pump is started and can take the chamber, after some hours of pumping, to pressures in the order of 10^{-7} mbar.

NKN Target Preparation

The preparation of the Na_{0.5}K_{0.5}NbO_3 targets used throughout the experimental procedure consisted of the following steps [12]:

1. Solid–state reaction with stoichiometric ratios of starting materials (potassium carbonate, sodium carbonate and niobium oxide)
2. Mixing of the powder
3. Calcination at 920°C for 4 hours
4. Pelletizing of the samples
5. Sintering at 1000°C for 4 hours

The calcination and sintering temperatures were chosen so as to obtain dense and single-phase NKN.

Experimental Procedure

In order to better understand the influence of oxygen pressure and substrate temperature on the thin films’ characteristics, the two parameters were treated individually. Anticipating that the oxygen pressure would reduce the flow of material from the target to the substrate, we started by reading with an oscilloscope the voltage generated across two electrodes by the collision of charged species with the substrate, during a laser pulse and for different values of oxygen pressure.
Deposition of samples began after that initial step. The first series of samples (NKN 20-25), studied the effects of pressures from 0.1 to 0.3 mbar in steps of 0.1 mbar on the morphology of the deposited films. The second series (NKN 27-32), continued this study but for lower pressures, from 0 to 0.1 mbar in steps of 0.02 mbar.

Once the analysis of the pressure parameter was complete, a series of new samples (NKN 35-42) intended to investigate the effects of temperature began. In order to do this, a pressure value of 0.2 mbar was selected as due to the conclusions drawn from the two previous steps and all samples belonging to this new series were deposited with this value of pressure. Even though this new series ran only from 450ºC to 600ºC, data from the older series which had been deposited at 400ºC (20-25) and 300ºC (27-32) was also used in the comparison.

This analysis of morphology was compounded with analysis of structure via XRD, sample composition via EDS, transmission, reflection, absorption and ellipsometry spectra with estimation of the band gap and the thickness of the films and C-F, R-F and loss tangent measurements.

Samples were mostly deposited over a substrate with a layer of Pt 150nm thick on top of TiO2 (10nm), SiO2 (300nm) and Si. However, in certain cases simultaneous depositions on sapphire were also carried out.

5 Results and discussion

Fig. 5.1 – Ionic current measurements.

Fig. 5.1 makes apparent that even a small increase in oxygen pressure from 0.02 mbar to 0.1 mbar can affect drastically the flow of ablated material from the target to the substrate. Fig. 5.2, however makes it clear that an increase in oxygen pressure leads to a more uniformly covered surface with less of the defects that comprise ferroelectric properties according to [13].
A compromise value for pressure had to be reached so as not to overly decrease the deposition rate but also not to lose uniformity. The chosen value was 0.2 mbar, due to the fact that it was high enough for the concentration of defects to have decreased dramatically and it was at this value of pressure that the next samples were deposited when the effects of temperature were studied by depositing samples at different temperatures.

Fig. 5.3 compares samples deposited at different temperatures but with an oxygen pressure of 0.2 mbar. This SEM image is evidence that the formation of a crystalline phase depends heavily on substrate temperature. Moreover, the fact that NKN 35, which was deposited at 500°C exhibits partial crystallization but the surface of NKN 38, deposited at 530°C, is fully covered with crystallites, suggests that a critical temperature must exist in the 500°C-530°C interval. NKN 42a, deposited at 600°C is fully covered by well-defined crystals with lengths of up to 500nm.
EDS measurements revealed, however, significant discrepancies in the stoichiometric ratios of Na, K and Nb, as can be seen in Table 5.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na</th>
<th>K</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>20a</td>
<td>0.52</td>
<td>0.48</td>
<td>2.41</td>
</tr>
<tr>
<td>30a</td>
<td>0.52</td>
<td>0.48</td>
<td>1.80</td>
</tr>
<tr>
<td>42a</td>
<td>0.58</td>
<td>0.42</td>
<td>2.46</td>
</tr>
</tbody>
</table>

Table 5.1 - Stoichiometric ratios for NKN 20a (400°C), 30a (300°C) and 42a (600°C).

Clearly enough, a disproportionate volatilization of the species Na and K took place, as Nb in these films has roughly twice the stoichiometric ratio Nb in the target. One possible explanation for this deviation lies in the slow cooling process after deposition [32]. Since the substrate takes several minutes to cool down to room temperature, the substrate is kept for some time at temperatures at which Na and K can volatilize.

Optical Transmission, absorption and reflection measurements revealed band gaps in the 3.58-3.86 eV range and with ellipsometry film thicknesses of up to 495nm were estimated.

C-F and R-F measurements confirmed the expectations laid by the EDS results. The films were found to be highly resistive and leaky and exhibited significant losses. Space constraints would compress the graphs and make them difficult to visualize. For this reason these plots are displayed only in the full-length version of the thesis.

6 Future Work

This experimental work has addressed several parameters/deposition conditions that need to be optimized in order to grow good NKN films. However, a few issues remain, that future work should try to deal with.

Especially worthy of mention is the low power output of the Nd:YAG laser which causes the deposition process to take hours to complete what more powerful lasers can do in as little as 12 mins. In order to solve this problem and in keeping with the idea of trying to improve the experimental setup itself, in parallel with the experimental work, we started setting up a Kr excimer laser with a UV line of
248 nm built by Lambda-Physik. This task is ongoing but not yet finished.

The filament used as heater inside the chamber can only heat the substrate up to 600ºC before the applied voltage causes it to deteriorate and for this reason research on the effects of temperature could not move past this value.

A more capable cooling system could dramatically reduce the time it takes to cool from deposition temperatures to room temperature which would lead to reduced loss evaporation of Na and K and thus to more stoichiometric films and hopefully ferroelectric behavior.

As for different directions of research, an interesting suggestion can be found in [15]. This publication reported an alternative approach to the problem of substrate temperature for films deposited by RF Magnetron Sputtering. This article describes how films grown at 300ºC and post-annealed at 800ºC in an atmosphere of Na2O actually exhibited better ferroelectric properties than films grown at higher temperatures and it would be insightful to try replicate these results with PLD.

Also interesting would be to investigate ways to improve the ferroelectric properties of NKN while keeping with non-hazardous nature of this ceramic. LiNbO3-doped NKN seems to be capable of doing just that [12].

References


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