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To cite this article: Scott Harada and Paul Muralt 2010 IOP Conf. Ser.: Mater. Sci. Eng. 8 012004

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Pulsed laser deposition of KNN-based ferroelectric thin films on platinised Si substrates

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Abstract. In this paper we report work on a modified potassium sodium niobate composition that has the potential to replace PZT for piezoelectric thin film applications. Pulsed laser depositions were undertaken on platinised Si substrates. The resultant films were found to be well-oriented in the [100] direction and almost phase-pure. TEM analysis of film cross-sections revealed the grain structure to be highly columnar. Values for $P_s = 3.8$ $\mu$C/cm$^2$ and $E_c = 20$ kV/cm were derived from polarisation hysteresis measurements for a 3.2 $\mu$m thick film. Finally, piezoresponse force microscopy was used to map the local piezoelectric activity down to the level of individual grains in the film.

1. Introduction

Research into lead-free alternatives to the commonly used piezoelectric material PZT continues unabated. One particularly attractive and useful group of materials are the alkali niobates which, depending on composition, display favourable electro-optical, electro-mechanical and acousto-optical properties. Saito et al. recently demonstrated the exceptional piezoelectric properties associated with (K,Na)NbO$_3$–LiTaO$_3$–LiSbO$_3$ perovskite solid solutions, in ceramic form [1]. Consequently, this has driven researchers to investigate the possibility of such behaviour in thin film form.

To the best of our knowledge thin films of $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_3$ (hereafter abbreviated to NKLNTS) have thus far only been deposited on single-crystal SrTiO$_3$ substrates [2-4]. These provide an ideal basis on which to study epitaxial growth, due to a favourable lattice match between film and substrate. However they are impractical for use in actual devices due to their high cost. It is therefore important to investigate the growth of NKLNTS on substrates more suited to industrial applications. One such example, platinised Si, has found widespread use in the production of microsystems with PZT thin films and was therefore chosen as the subject of this study. The highly flexible PLD technique was used to deposit the films.

2. Methodology

PLD Targets were prepared using a conventional ceramic processing route. The precursor powders (K$_2$CO$_3$, Na$_2$CO$_3$, Li$_2$CO$_3$, Nb$_2$O$_5$, Ta$_2$O$_5$ and Sb$_2$O$_5$ sourced from Alfa-Aesar, Fluka or Aldrich with...
purities ≥ 99.7 %) were dried in an oven at 200 °C prior to weighing. Stoichiometric quantities of the powders, to form the (K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_{3} composition, were mixed for 24 hr in a flask containing anhydrous ethanol and ZrO_{2} balls. Calcination was then conducted in air at 880 °C for 4 hr. The calcined powder was crushed using a pestle and mortar and then mixed for a further 24 hr before being pressed into pellets that were 32 mm in diameter and 4 mm thick at a pressure of 37 MPa. After sintering at 1135 °C for 4 hr in air, the pellets were approximately 85% dense. XRD analysis confirmed the phase purity of the target, with the only peaks visible assignable to a pure pseudocubic, perovskite structure.

Films were deposited using a custom built PLD chamber in combination with an ArF excimer laser that had an output wavelength of 193 nm. The laser fluence, calculated from the beam spot size, was 3 Jcm^{-2} and the repetition rate 5 Hz. Platinised Si substrates (Pt(111)/TiO_{2}/Ti/SiO_{2}/Si(100)), approximately 1 cm^{2} in area, were used throughout the investigation. The substrates were mounted on a Neocera substrate holder and heated to between 500 – 700 °C, under an O_{2} partial pressure of between 0.05 – 0.6 mbar, during the depositions.

Analysis of film crystallography and microstructure was conducted using powder XRD and TEM. Electrical characterisation was achieved by evaporating circular (σ = 170 µm) Au top electrodes onto the surface of the film to create capacitor structures. Verification of the ferroelectric nature of the films, on the macro- and nanoscale, was achieved using a Sawyer-Tower circuit and piezoresponse force microscopy, respectively.

3. Results

3.1. Film microstructure and phase

Films deposited onto platinised Si substrates were found to be highly (100)-oriented (Figure 1a). A small quantity of a Nb-rich impurity phase, thought to correspond to the pyrochlore compound K_{x}Nb_{y}O_{16} (JCPDS PDF card no. 28-0788), was also present. The films were generally composed of columnar grains, which resulted in a rather high surface roughness (Figure 1b).

![Figure 1](image.png)

**Figure 1.** a) XRD data for a 3.2 µm NKLNTS film deposited on a platinised Si substrate at 700 °C under an O_{2} partial pressure of 0.6 mbar (red labels correspond to those peaks assigned to the NKLNTS phase), b) TEM cross-sectional image of a typical NKLNTS film.
3.2. Ferroelectric and piezoelectric properties

The high volatility of the A-site elements in KNN-based materials can lead to vacancies forming in the lattice under the elevated temperatures necessary for deposition. This can be problematic when attempting ferroelectric measurements due to large leakage currents which are a result of the p-type conductivity of A-site deficient films. Consequently, it was only possible to obtain measurements from capacitor structures containing films of several micrometres in thickness. Loops acquired from films with reduced thickness were non-saturated and exhibited lossy dielectric behaviour. The coercive field and spontaneous polarization values, derived from the loop of a 3.2 \( \mu \)m film, were 20 kV/cm and 3.8 \( \mu \)C/cm\(^2\), respectively (Figure 2). These values compare well with those of Saito et al. who deposited NKLNTS films of approximately the same thickness on SrRuO\(_3\)-coated SrTiO\(_3\) substrates [2].

![Figure 2. Polarisation hysteresis loop for a 3.2 \( \mu \)m NKLNTS film deposited on platinised Si.](image)

Analysis of the piezoelectric nature of individual NKLNTS grains was achieved using piezoresponse force microscopy. This technique utilizes a modified AFM system to probe the localized piezoresponse phase and amplitude signals from regions on the film surface. Figure 3 shows the topography and associated out-of-plane piezoresponse signals from a 1 \( \mu \)m \( \times \) 1 \( \mu \)m area of a 3.2 \( \mu \)m thick NKLNTS film. From the topographical image the average grain size appears to be in the region of 100 nm. White and dark regions in the phase image represent domains with polarization vectors facing into and out of the film plane, respectively. Regions with intermediate contrast are either weakly or non-piezoelectric or in-plane polarized. The greater proportion of white to dark regions might be indicative of self-polarization in the film. In the amplitude image, white regions represent areas of high piezoelectric activity, whilst the opposite is true for dark regions. The removal of clamping is one possible explanation for the large response of certain grains, especially since the surface roughness of the film is known to be high.
**Figure 3.** a) Topography and associated out-of-plane piezoresponse b) phase and c) amplitude signals from a 1 μm × 1 μm region of a 3.2 μm NKLNTS film on platinised Si.

4. Conclusions

We have demonstrated the possibility of depositing (100)-oriented NKLNTS films on platinised Si substrates via PLD. A small quantity of a pyrochlore impurity phase was also detectable in films analysed by XRD. The grain microstructure was generally found to be highly columnar which had adverse consequences for the surface roughness of films. Macroscale electrical measurements were hampered by large leakage currents. Nonetheless, it was possible to record ferroelectric polarisation hysteresis loops from a film that was 3.2 μm thick. The spontaneous polarization and coercive field of this film were comparable to those of similar films deposited on SrRuO$_3$/SrTiO$_3$ substrates. This result opens up the possibility of integrating piezoelectric NKLNTS thin films with industry standard Si substrates.

5. Acknowledgements

The authors wish to thank Dr. Cosmin Sandu for TEM measurements and the EU for providing financial support as part of the 3D-DEMO project (STREP 033297).

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