Solution-processed lead-free piezoelectric materials and devices

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Abstract

Sensors, actuators, transducers in micro-electromechanical systems (MEMS), technologies using micro-optical devices such as atomic force microscopes (AFM), infrared (IR) detector arrays etc., are used to connect mechanical changes with changes in the charge state of the active piezoelectric layer. For ubiquitous deployment of MEMS-based vibration energy harvesters in distributed flexible sensors, fabrication processes must be cost-effective and environmentally friendly. Lead zirconium titanate (PZT) and other lead-based materials such as lanthanum-doped PZT (PLZT), $Pb(Mg_{1/3}Nb_{2/3})O_3\,PbTiO_3$ (PMN-PT) dominate the market for piezoelectric materials due to their excellent electromechanical properties. However, the presence of lead in these materials presents an environmental and health challenge that limits the regulatory approval for several devices. Within the overall history of electrically active ceramics, technological interest in the perovskite potassium sodium niobate ($K_xNa_{1-x}(NbO_3)$ KNN) has grown over the previous decade due to the high electromechanical coefficients (d_{33}). The performance of KNN compares favourably with the performance of industrially relevant but environmentally deprecated materials composed of lead perovskites like PZT, PMN-PT, etc.

This dissertation focuses on the synthesis and deposition process for fabricating uniform amorphous thin (~ 70 nm) unannealed films of potassium sodium niobate (KNN). This study employed three different ratios of sodium and potassium in order to study the stoichiometric effects of composition on the final film and its piezoelectric properties. The study focuses on reducing the overall thermal budget of processing from materials synthesis to fabrication of

the device. This PhD aimed to explore and employ lead-free piezo-active material to fabricate flexible devices such as energy harvesters. The low thermal footprint of the process is likely to significantly lower the cost of devices requiring high-performance piezoelectric materials, which are also environmentally friendly. The impact of electric-field assisted densification of a low temperature solution-processed piezoelectric inorganic film (potassium sodium niobate, KNN) has also been investigated. A concentrated ($K_xNa_{1-x}(NbO_3)$, x=0.5) sol of the material was drop casted on an insulating SiO_2 substrate with two electrodes deposited in a lateral diode geometry. Surface metrology and compositional scans on the post-processed film revealed a cracked morphology with apparent densification and a stoichiometric shift from 51:49 to 31:69 (K:Na). An image processing method was used on electron microscopy images to estimate a ~20 % volume reduction over an area of 400 μm^2 using topographical film data. Further, the system was simulated using a finite element method on a 3D model system, and the simulated electric field lines appear to explain the observed post-annealed densified profiles.

A modified method for the estimation of electromechanical coefficient (d_{33}) of thin film has been developed for the characterization of a solution-processed piezoceramic thin-film $M\pi M$ parallel-plate capacitor structure using capacitance-voltage measurements. Electrical loading was applied to the capacitor to stimulate out-of-plane longitudinal and transverse elongation. The results were validated using FEM-based modelling and compared with several measurements in literature, including piezoresponse force microscopy-based measurements, which are generally considered unreliable due to strong electrostatic interactions between the tip-cantilever, and the charged sample surface, wherein such artefacts result in the overestimation of the electromechanical response of the material under investigation.

Further, a metal-piezo-metal (MπM) based single-pixel (sensing element or energy harvester) 1x1 cm energy harvester was fabricated using solution-processed potassium sodium niobate films on aluminium-coated polyethylene terephthalate (PET) substrates. Initial measurements using a full-wave diode bridge rectifier circuit show a real-time response time of ($\sim$0.13 sec) on the application of variable pressure. The magnitude of the voltage signal generated is $\sim 40\,\mathrm{mV}$ greater than the expected rectification drop of $\sim 1.4\,\mathrm{V}$, suggesting significant charge transduction in the harvester.

In summary, in the course of the doctoral work, material development, material characterization, device design, device fabrication, and characterization involving solution-processed lead-free materials have been carried out.