1. Introduction

Piezo- and ferroelectrics are an integral part of modern technological society, with major applications in sensor and actuator technology, and emerging applications in nonvolatile memory, bandpass filters and imaging technology. The world market is estimated to have passed $20 billion in 2018, and is steadily increasing. Current materials of choice are lead based perovskites, commonly PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) and PbMg$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PMN-PT). The popularity of these materials stems from facile preparation, low cost, highly applicable physical properties, and high tunability. They can be selectively varied by altering cation stoichiometry across the morphotropic phase boundaries of the KNbO$_3$–NaNbO$_3$ solid solution. The films are obtained as highly oriented on Pt (111)|Si (100)-substrates after annealing at temperatures as low as 550 °C. They exhibit converse piezoelectric effects with magnitudes in the order of 550 pC N$^{-1}$ at 1000 Hz. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

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boundaries throughout the boule. More problematic, the cation composition is hard to control throughout the growth process, leading to gradients in the K/Na-composition and thereby non-uniform piezoresponse. The current approach is to produce large boules, and then cut out a crystal with the correct stoichiometry, which is tedious, ineffective and expensive.

Deposition of thin films of KNN has been as achieved by pulsed layer deposition (PLD), metal–organic chemical vapor deposition (MOCVD), and sol–gel coating. PLD typically requires elevated growth temperatures (>600 °C) with challenges in control of cation composition. Uniform, single-deposition PLD growth over larger areas (>10 cm) remains yet to be overcome. MOCVD growth suffers from high growth and/or annealing temperatures (>800 °C), which make monolithic integration on functional devices difficult. Controlling the K:Na-uniformity is likewise challenging. Sol–gel methods may provide relatively uniform films over larger areas. Unfortunately, these tend to suffer from precursor pre-reactions, from crack formation due to shrinkage during solvent evaporation as well as carbon contamination often being detrimental to functionality.

Atomic layer deposition (ALD) is a layer-by-layer self-limiting thin film growth technique that offers high chemical uniformity and thickness conformality over large areas. It has traditionally been used to deposit high-K binary oxides and nitrides for microelectronics applications, and is implemented in industry for ultra-small node transistors in processing units. The available chemistry for ALD has increased strongly over the last years, and the technique can now be used for depositing nitrides for microelectronics applications, and is implemented in industry for ultra-small node transistors in processing units. The current approach is to produce thin films of complex oxides by ALD is normally carried out by combining binary oxide processes to form a supercycle process. In the case of alkali metal containing films, this is not as straightforward, since the alkali metal binary oxides are not stable. In other words, the stoichiometric ratios between Na/K and Nb must be tuned simultaneously. This is carried out by growing films with gradually increasing alkali metal content, while monitoring the deposited Na/K to Nb cation ratio. In this study, we focused on the stoichiometric 1:1 ratio between alkali metal and niobium in correspondence with the wanted perovskite type phase. As the structure and chemistry of the two precursor systems (tert-butoxide vs ethoxide) is very different, the 1:1 ratio is not achieved at a 1:1 pulsed ratio between the precursors, but at a 2:7 ratio between AO′Bu (A = Na, K) and Nb(OEt)₅. The applied process is described by

\[
\begin{align*}
3 \times [\text{Nb(OEt)}_3 + \text{H}_2\text{O}] + \text{AO′Bu} + \text{H}_2\text{O} & \\
4 \times [\text{Nb(OEt)}_3 + \text{H}_2\text{O}] + \text{AO′Bu} + \text{H}_2\text{O} & \\
\end{align*}
\]

Here, \(n\) describes the full supercycle, and the film thickness is determined by \(n\) alone. With this study, we have applied ALD to grow thin films of KNN with very high chemical conformality as low as 250 °C. The films are stoichiometrically uniform as grown in a 30 cm chamber, proving the ability of successful deposition over large areas, i.e., for many devices. The cation stoichiometry is tuned at a 1% level, giving sufficient control to obtain compositions close to the MPB. The current growth rate of 100 nm h⁻¹ is likely to benefit further from future optimization. The process is highly reproducible, and easily implemented in batch processing at industry scale. These findings hopefully represent a giant leap toward abolishing the lead dominance of piezo- and ferroelectrics.

2. Results and Discussion

2.1. Conformal Growth

The deposition of complex oxides by ALD is normally carried out by combining binary oxide processes to form a supercycle process. In the case of alkali metal containing films, this is
growth per cycle is slightly lower for high K-concentration, without this affecting the overall composition.

Considering the pulsed versus deposited concentration of Na and K in \( A \), we observe the expected (close to) linear trend over the whole composition range, see insert to Figure 2. The slight convex curve originates from a small difference in growth per cycle between the (imagined) binary sodium and potassium oxide systems. A detailed study was done for pulsed Na:K compositions close to 50:50, Figure 2. The linear trend represents an important result as it shows that the composition can be tuned at the percent level and thereby to control the Na:K ratio very close to the MPB. We describe below detailed results for the 50:50 deposited samples as achieved by using a 48:52 pulsed K:Na-ratio.

A limiting factor for most thin film deposition technique is lack of the ability to maintain cation uniformity over a large deposited area. Such abilities are obviously very important when considering potential industrial upscaling. The larger the effective uniform area provided by the process; the more devices can be coated at any given time. We have quantified the compositional homogeneity by utilizing the whole ALD reaction chamber (\( \Phi = 30 \) cm), followed by mapping of the Na:K-ratio for substrates situated at five different locations in the chamber (Figure 3).

The cation stoichiometry of the films was determined by XRF and X-ray photoelectron spectroscopy (XPS). XPS had a small probe size of 3 mm, allowing for a quite detailed geometrical mapping. XPS was currently used to quantify the relative ratio between Na and K, whereas XRF was used to determine the stoichiometry on an absolute scale.

Figure 4 shows a map of the Na:K cation ratio distribution over a 3 \( \times \) 3 cm\(^2\) substrate placed in the middle of the chamber. The ratio is measured at 25 different locations, spaced minimum 6 mm apart. The stoichiometry measured by XPS varies between \( K_{0.48}Na_{0.52}NbO_3 \) and \( K_{0.52}Na_{0.48}NbO_3 \), with all points within 2\( \sigma \) of \( K_{0.50}Na_{0.50}NbO_3 \left( \sigma = \frac{1}{N} \sum_{i=1}^{N} x_i - \mu = 0.014 \right) \). As there is no evident directional dependence, we assume that the variation represents uncertainty in the measurements, rather than being a physical manifestation. In any case, the variation is so small that the functional properties over the observed compositional interval will be close to equal, i.e., we expect \( \Delta d_{33} < 1\% \).\(^{[23]} \)

The total variation across the whole reaction chamber is shown in Figure 5 based on eight depositions. The ellipses are constructed by taking the maximal cation variation (x-direction) and the uncertainty in the XPS quantification (y-direction). The eight depositions were done with the exact same parameters (pulsed K:Na = 50:50) in order also to investigate reproducibility. The maximum variation across all directions in the 30 cm chamber is \( \approx 2 \) cat% when comparing eight depositions. This is well within acceptable values in terms of functionality. The obtained average value is 51.99 \( \pm \) 0.55 cat% Na. We estimated

\[ \sum \sigma = 1.014 \]
the expected variation in cation stoichiometry if replacing one Na-pulse with a K-pulse or vice versa (red dotted box in Figure 5). This shows that the stoichiometry of the deposited films is highly reproducible, and that the cation concentration can be fine-tuned on the single pulse level.

Note that a passivation deposition step of 22 nm Nb$_2$O$_5$ (500 cycles of Nb(OEt)$_5$ + H$_2$O) was added in between every KNN-iteration, to avoid memory effects from the preceding deposition.[22] This slightly slows down any batch processing, however, still two depositions of micrometer thickness could be facilitated per day, per reactor. We expect that significant process effectivization can be achieved by optimizing precursor temperature and pulse- and purge times.

2.2. Structure and Functionality

The structure and functionality were studied of uniform films, K$_{0.52}$Na$_{0.48}$NbO$_3$ deposited on Pt(111)@Si(100). The Pt(111) surface facilitates epitaxial growth of KNN. Best lattice match is achieved for the slightly shorter $a$ and $b$ lattice parameters, hence we expect tetragonal (or orthorhombic but very close to tetragonal) KNN with the longer $c$-axis predominantly oriented perpendicular to the substrate plane (KNN(001)||Pt(111)||Pt(110)||Si(100)||Si(001)).

The obtained films are X-ray amorphous as deposited at 250 °C, which is typical for low-temperature chemically deposited thin films. Crystallization was achieved by postannealing at 550 °C for 30 min. The required annealing temperature is low compared to treatments required for other techniques, and will facilitate monolithic integration for most applications.

X-ray diffraction (XRD) shows sharp reflections from oriented KNN, as well as from Pt(111) and Si(100) (Figure 6a). No other reflections are observed, which indicates that the film is fully oriented out-of-plane, and that no secondary crystalline phases are present. However, taking a closer look at (002) it is evident that it is at least split in two. A two Gaussian model gives the best fit for the reflection, however we cannot rule out that the films are orthorhombic and that a third reflection is present. These two reflections correspond to KNN(002) and KNN(200), with a difference in unit cell parameters of ≈0.05 Å, in accordance with expectations. A corresponding split is not observed for the KNN(100/001)-peak due to resolution limitations. The weighted (integrated) area after peak deconvolution of KNN(002) and KNN(200) indicates a 1:15 ratio, meaning that ≈7% of the KNN crystallites are (100)-oriented. This is not detrimental to function, however, the situation may nonetheless possibly be avoided by post-annealing in an electric field.[24]

We probed the piezo-/ferroelectric functionality of the KNN films by using in situ XRD (at SNBL@ESRF, Grenoble, France) upon perturbating the material by means of an electric field. The setup is described in a previous publication.[25] This allows careful identification of the $c$- and $a$-axis of the cell under electric load. The bottom Pt-layer is contacted in a corner of the specimen that was masked during deposition and hence works...
as the bottom electrode. Gold contacts are deposited on the surface of the KNN film, working as top contacts. Figure 7 shows the relative change in unit cell parameters in terms of degree of tetragonal distortion as a function of applied electric field. We observe a major, ≈40%, change in the degree of tetragonal distortion upon perturbation by an electric field. When the field is applied perpendicular to the surface and strain is measured along the c-axis, the generalized equation for the induced strain as well as hysteresis on increasing and decreasing fields (coercive field, $H_c \approx 40\%$). The latter crude estimate is higher than bulk literature values, however, this is not uncommon for thin film ferroelectrics due to domain wall pinning and strain-related effects.[26–28]

The change in tetragonal distortion upon perturbation by an electric field can be transformed into an estimate of the converse piezoelectric coefficient, by taking only the strain induced component along the c-axis into account. When the field is applied perpendicular to the surface and strain is measured along the KNN c-axis, the generalized equation for the induced strain

$$\varepsilon_1 = d_{33}E_1$$

Using the absolute values of the elongation in the c-axis and the potential across one unit cell (averaged to 1.58 millistrain V$^{-1}$ for a series of measurements), the converse piezoelectric coefficient is estimated to $d_{33} = 105 \text{ pm V}^{-1}$ (or $\text{pC N}^{-1}$). It should be noted that this is a crude estimate, as variations in the cell-parameters of magnitude in the $0.001 \text{ Å}$ range is close to the resolution limit of the diffraction measurements. The value is nonetheless close to previously reported values for KNN thin films, and we believe this serves as proof-of-concept that atomic layer deposited thin films of KNN preserve very attractive functionality.

### 3. Conclusion

Thin films of K$_x$Na$_{1-x}$NbO$_3$ with very high structural and chemical uniformity is deposited by atomic layer deposition. In literature, the challenge to receive a uniform K/Na-ratio throughout single crystals or crystalline films has been considered difficult to overcome. We have currently proved successful deposition of KNN with controlled composition and excellent chemical uniformity on the percent level for a reaction chamber with diameter $\Omega = 30 \text{ cm}$. The uniformity has been reproduced with high accuracy, with only minor variations in chemical composition and thickness. The adopted deposition temperatures are much lower than for competing thin film techniques and the required post-annealing crystallization was achieved at $550^\circ\text{C}$, i.e., at temperatures sufficiently low for facilitating monolithic integration into devices. The favorable structural and functional properties of KNN were confirmed through diffraction analysis, both ex situ and in situ under perturbation by an electric field. Based on these experiments we have estimated a converse piezoelectric coefficient $d_{33} = 105 \text{ pm V}^{-1}$, which is in agreement with previously reported values.

In our opinion the results clearly show that the cation uniformity issue can be overcome by using ALD. This opens for further work on chemical substitutions into the KNN matrix to obtain films with enhanced functional properties that may match those of lead-based piezoelectrics. We consider this as a large step on the way to abolish the lead dominance in piezoelectrics.

$$\begin{bmatrix} 
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6 
\end{bmatrix} = \begin{bmatrix} 
d_{11} & d_{12} & d_{13} \\
d_{21} & d_{22} & d_{23} \\
d_{31} & d_{32} & d_{33} \\
d_{41} & d_{42} & d_{43} \\
d_{51} & d_{52} & d_{53} \\
d_{61} & d_{62} & d_{63} 
\end{bmatrix} \begin{bmatrix} 
E_1 \\
E_2 \\
E_3 \\
E_4 \\
E_5 \\
E_6 
\end{bmatrix} \rightarrow \begin{bmatrix} 
0 & 0 & d_{11} \\
0 & 0 & d_{11} \\
0 & 0 & d_{11} \\
0 & d_{15} & 0 \\
d_{15} & 0 & 0 \\
0 & 0 & 0 
\end{bmatrix} \begin{bmatrix} 
E_1 \\
E_2 \\
E_3 
\end{bmatrix}$$ (2)
All depositions were carried out using potassium tert-butoxide (KOtBu, Aldrich, 97%), sodium tert-butoxide (NaOtBu, Aldrich, 97%), and niobium ethoxide (Nb(OEt)5, Sigma Aldrich, 99%) as metal precursors. The tert-butoxides were supplied from HS 300 metal bubbler sources heated to 150 and 140 °C for KOtBu and NaOtBu, respectively. Nb(OEt)5 was supplied from an open glass boat in a HS 500 source maintained at 68 °C. Deionized H2O was used as the oxygen source, supplied from a glass bubbler maintained at room temperature. Pulse times were set to 3, 3, 2, and 0.25 s for KOtBu, NaOtBu, Nb(OEt)5, and H2O, respectively. All purge times were set to 2 s. These deposition parameters were chosen to obtain self-limiting growth as previously reported.[22]

The films were deposited on 1 × 1 and 3 × 3 cm2 Si (100) substrates for characterization of thickness, conformality, and composition. Selected films were deposited on Pt(111)/Si(100) (SINTEF, Norway) for characterization of electrical properties.

The thin film thickness was measured using a J. A. Woollam alpha-SE spectroscopic ellipsometer in the range of 390–900 nm. A Cauchy-function was successfully used to model the collected data.

Rapid thermal annealing was carried out in an OTF-1200X (MTI Corp.) furnace heated by halogen lamps. A ramp rate of 10 °C s−1 was employed to reach the set temperature.

X-ray diffraction measurements were performed on a Bruker AXS D8 Discover diffractometer equipped with a LynxEye strip detector and a Ge (111) focusing monochromator, providing Cu Kα radiation (λ = 1.5406 Å).

In situ determination of unit cell variations under perturbation by an electric field was carried out with synchrotron X-ray diffraction at the Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility (BM01 - SNBL@ESRF) in Grenoble, France. BM01 is a bending magnet end station. A monochromatic beam with wavelength 0.6745 Å was employed. The setup is described previously in literature.[23]

Average chemical composition was analyzed using a Panalytical Axios Max Minerals XRF system equipped with a 4 kW Rh-tube. The system is running with Omnian and Stratos options for standardless measurements.

Complimentary measurements of composition and spatial cation distribution were carried out with XPS, using a Thermo Scientific Theta Probe Angle-Resolved XPS system. The instrument is equipped with a standard Al Kα source (hv = 1486.6 eV). Pass energy values of 200 and 60 eV were used for survey spectra and detailed scans, respectively. The data was corrected for shifts using the peak from adventitious carbon (binding energy = 284.8 eV) as reference.

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Conflict of Interest

The authors declare no conflict of interest.