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High throughput method for $K_{0.5}Na_{0.5}NbO_3$ thin films preparation by chemical solution deposition

C. Schroeter[a,b,*], B. Wessler[a], L.M. Eng[b]

[a] *Siemens AG, Otto-Hahn-Ring 6, 81739 Munich, Germany*
[b] *Technische Universität Dresden, George-Bähr-Str. 1, 01069 Dresden, Germany*

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Abstract

A high throughput method for synthesis and characterization of ferroelectric thin film libraries prepared by chemical solution deposition was developed. With a throughput of over 100 samples of different composition/day, it is possible to screen vast composition fields in a manageable amount of time. The method was applied to films of the binary $KNbO_3$–$NaNbO_3$ system. Structured Pt/SiO_2/Si wafers were used as substrates. Samples of 450 nm thickness with remarkable dielectric properties and pure perovskite phases were obtained by optimizing the composition with respect to the K/Na-ratio, and by identifying the ideal amount of alkali-metal excess added to the precursor solutions.

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1. Introduction

Ferroelectric materials are of great technological interest due to their electric, pyroelectric, electrooptic, and piezoelectric properties. Thin films of ferroelectric materials offer a way to build miniaturized devices like memories, sensors and MEMS.[1] The wide field of application demands intensive research for the development of new ferroelectric thin film materials and their tailoring according to the specific demands.

High throughput experimentation (HTE) can substantially reduce research costs through automated sample preparation and characterization. A HTE route for the development of ferroelectric thin films by chemical solution deposition (CSD) was established, which is a cost-efficient alternative to gas-phase deposition techniques. Also, CSD allows for exact stoichiometry control and effortless incorporation of dopants on the molecular level.

Lead zirconate–titanate (PZT) is a ferroelectric material used in a wide range of applications both in the form of bulk ceramics and thin films.[2] While PZT exhibits excellent piezoelectric and ferroelectric properties, it constitutes an environmental burden due to the lead content. In bulk ceramics, sodium-potassium-niobate $(K_xNa_{1-x})NbO_3$ (KNN) shapes up to be a promising lead-free substitute for PZT.[3] At room temperature, the crystal structure of both end members of the KNN system is orthorhombic, $KNbO_3$ (KN) being ferroelectric while $NaNbO_3$ (NN) is antiferroelectric.[4] For $x \approx 0.5$, KNN shows a morphotropic phase boundary (MPB), where piezoelectric and ferroelectric properties increase as compared to pure KN. While most of the current research activities are devoted to bulk ceramic KNN and its doped derivatives, thin film preparation of these materials is scarcely encountered.

A few reports exist on the preparation of KNN thin films by vapor phase deposition techniques onto various substrates[5,6] by using pulsed laser deposition or sputtering methods. Only one report was found reporting on the application of CSD techniques to KNN thin films.[7] On amorphous or metallic substrates, phase impurities and deviations in the KNN thin film stoichiometry were frequently encountered. In the case of KN,[8–10] the substrate seems to play an important role affecting the phase formation and growth of the perovskite film; suitable substrates were reported with $SrTiO_3(1\,0\,0)$, $MgAl_2O_4$, or Al_2O_3, where the lattice parameters are matching those of KN, and exert a catalytic effect on phase formation. Hence, these substrates may also be suitable for the preparation of KNN[6] thin films. However, from a technological point of view, conductive substrates are preferable, as electric fields can directly be coupled into the film.

We report here the preparation of KN, KNN, and NN thin films on Pt/SiO_2/Si substrates by a high throughput CSD

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[*] Corresponding author at: Siemens AG, Otto-Hahn-Ring 6, 81739 Munich, Germany.
E-mail address: christian.schroeter.ext@siemens.com (C. Schroeter).

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method, as well as on the electrical characterization of these films.

2. Automated library synthesis

This section describes the general procedure of the HTE-CSD-route from preparation of precursors, their automated mixing and deposition of these liquids to a structured Si-wafer to form ceramic thin films. Experimental details concerning the present study are given in Section 4.

For the high throughput CSD experiments, a set of 30 elementary sols, each containing one specific element, was developed.[11] They consist of an organic compound of this element, which is dissolved in mixtures of ethanol, isopropanol and propionic acid, in rare cases supplemented by stabilizing agents. Stabilizing agents are only used, whenever the elementary sols are not stable at ambient conditions for at least 5 h, which is roughly the time needed for this experiment. These precursors are miscible at arbitrary ratios without precipitation or gelation.

For scanning a material system containing *n* elements, usually only a small subset of the corresponding *n*-dimensional composition space is of interest, due, for example, to the restriction to stoichiometry or theoretical considerations. To screen this subset of interest, a small number of boundary compositions (BC) are manually prepared by mixing the elementary sols in the desired ratio. The BCs are representing the “corners” of the selected subset. Hereof, 90 mixed sols are composed by our liquid pipetting robot (see Fig. 1a) according to the chosen library design, which determines the step width between the BC, and hence the exact composition of the 90 compounds. The use of BCs makes it possible to be very flexible in the design of experiment, despite the fact that the number of library designs has to be limited in order to facilitate programming and data evaluation.

The substrates are 6 in.-silicon wafers, showing 90 circular sample areas, each measuring 8 mm in diameter, which are surrounded by grooves of 30 μm depth, structured by sandblasting. After structuring, substrates are coated with 1000 nm SiO_2 as the reaction barrier and 100 nm Pt to provide the bottom electrode.

After thorough automated mixing, the robot transfers small amounts of the 90 mixed sols to the sample areas on the substrate (Fig. 1b) by a “drop-coating” technique, as it is difficult to carry forward common CSD coating techniques like spin- or dip-coating. Excess liquid drains into the grooves, so the liquids do not admix.

The wafer is then pyrolysed at temperatures between 350 °C and 600 °C to remove organic residues. Coating and pyrolysis is repeated until the desired film thickness is reached. After the last coating, the wafer is exposed to temperatures between 600 °C and 800 °C for 15–60 min to promote crystallization.

3. High throughput characterization

Analysis of the phase composition of the thin films is a prerequisite for interpretation of the obtained dielectric properties. X-ray diffractometry (XRD) is carried out on a General Area Diffraction Detection System (D8 GADDS, Bruker AXS GmbH, Germany) by performing Θ-2Θ scans. As recording and interpretation of a diffractogram is relatively time consuming, XRD analysis is usually only done on few exemplarily chosen samples of the library, which are chosen such that they are evenly distributed throughout the material spread. The library, however, stays intact throughout the measurement.

The key parameter chosen for screening the material libraries is the permittivity at 10 kHz, as good piezoelectric properties go along with a high dielectric constant and low losses. All 90 samples of the library are screened. It is thus possible to observe trends within the compositional space and to confine the number of promising materials by means of a relatively simple technique. Calculating the relative dielectric constant ε_r according to Eq. (1), requires both capacitance C and film thickness d to

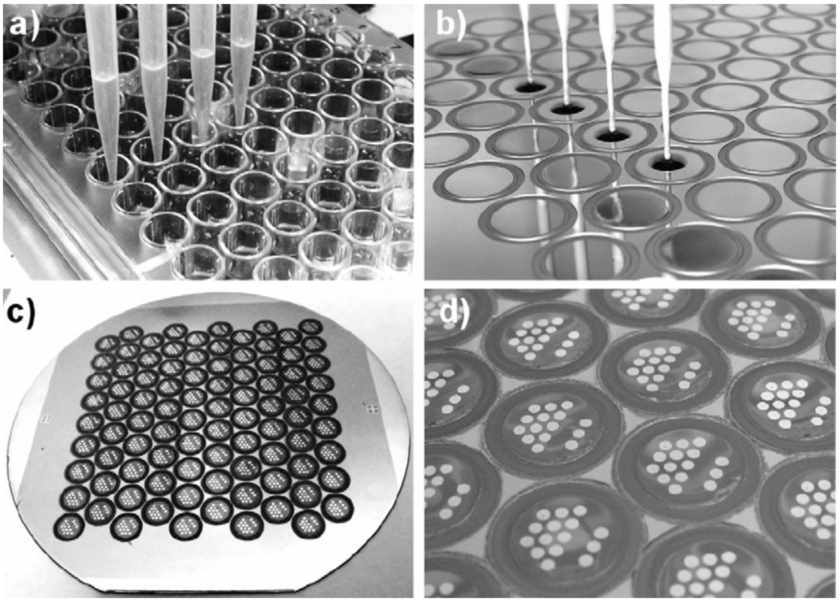

Fig. 1. Automated dosing and mixing of 90 mixed sols from the precursor solutions (a) and their application to the 90 sample areas of a structured 6 in. silicon wafer (b and c). Silver electrodes are evaporated onto the processed samples to permit electric characterization (d).

be known:

$$\varepsilon_r = \varepsilon_0^{-1} C \frac{d}{A} \qquad (1)$$

ε_r is the relative permittivity, ε_0 the permittivity of vacuum, C the capacitance, d the film thickness, and A is the electrode area.

These quantities are measured on15 spots/sample, that is, 1350 spots/library. This gives some redundancy in the case of erroneous measurements as may occur in the vicinity of film defects, and allows for checking consistency and averaging of the measured values.

The film thickness is measured by white light spectral reflectometry[12] combined with an automated *x*–*y*-table (vis-2000, Mikropack, Germany). Along with the film thickness, the refractive index and the roughness of the film can be extracted from every measurement. As automated fitting of multiple free parameters can lead to ambiguities, roughness and refractive index are calculated from few exemplarily chosen samples, where plausibility of the obtained values can be checked, and then kept fixed during the automated measurement. Along with the film thickness, the fitness, a parameter indicating the reliability of the measurement, is recorded for each of the 1350 spots.

To prepare wafers for electrical characterization, each sample is top-electroded by 15 evaporated silver spots, 1000 μm in diameter each (Fig. 1c and d). Non-covered areas were left over on every sample for characterization by methods that require no top electrode.

Electric measurements are carried out on a modular characterization unit. One module sequentially contacts the 1350 electrodes of the library. A measurement head containing 15 contacts is moved from sample to sample by an *x*–*y*–*z*-table (LTM 80, Owis, Germany), while individual electrodes are connected through by a switch system (7001, Keithley Instruments, Inc., USA). The second module is an impedance analyzer (Multi Frequency LCR Meter HP4275A, Hewlett Packard, USA) which measures the impedance at 10 kHz and 0.1 V amplitude. This device can readily be replaced whenever quantities other than the dielectric constant are of interest. Prior to calculating the dielectric constant of the samples from film thickness and capacitance, the measured data is filtered to eliminate erroneous data. For film thickness measurements, this is done by deleting measurements of exceptionally high fitness, whereas high dielectric losses indicate an erroneous capacitance measurement. The threshold values deciding upon deletion are not fixed, but depend on the typical values measured on the given library. From the remaining measurements, the relative dielectric constant is calculated. Details about synthesis and characterization are given elsewhere.[13]

4. Sodium-potassium-niobate thin films

Precursor solutions were prepared by dissolving Nb-, K- and Na-ethoxides (Chemat Technologies Inc., USA) in a mixture of absolute ethanol and 0.3 mol/l acetyacetonate (both received from Merck, Germany) to a final concentration of 0.15 mol/l. These sols are sufficiently stable at ambient conditions for the time of the experiment. Slight precipitation occurs during gelation, but was not found to be a major problem.

The library design shows three series of binary mixtures. In each series, the alkaline metal excess of KN (0–130% excess), KNN and NN (0–50% excess each), respectively, is progressively varied (see Fig. 3). Excess values are calculated with respect to the stoichiometric composition. In KNN the alkaline metal excess is chosen such that K:Na = 1:1in all KNN compositions. 1.5 μl of the mixed solutions are transferred to the wafer and pyrolysis is carried out at 550 °C on a hot plate with a heating rate of 30 K/min and a holding time of 2 min at the final temperature. After eight coatings, the wafer is directly put into a furnace, heated to 800 °C, and then taken out after 15 min of sintering.

XRD measurements on layers without alkaline metal excess showed dominantly Nb-rich phases other than perovskite. For KN films, pure perovskite material is found between 60% and 120% alkaline metal excess. The required excesses for KNN and NN were 22–50% and 15–40%, respectively (Fig. 2). Samples with pure perovskite phases generally show some degree of {1 1 0}-texture, as can be concluded from comparison with the peak intensities of KNN powder diffractograms. This {1 1 0}-texture is higher for Na-rich compositions, while in some KN films, a {1 0 0}-texture is sometimes found. A homogeneous increase of the lattice parameter with increasing potassium-content is observed.

The mean film thickness averaged over all spots is 450 nm and a refraction index of 2.0 is fitted to the spectra. The roughness of the KNN layers leads to 10% loss of intensity due to scattering. KN shows a higher roughness, NN a lower one. The electrical measurements show that the highest dielectric constants are found in pure perovskite thin films and are higher in KNN than in KN or NN (Fig. 3). The dielectric losses are between 20% and 40%, being the lowest in NN and the highest in KN. Losses can be reduced to 5% for all compositions upon

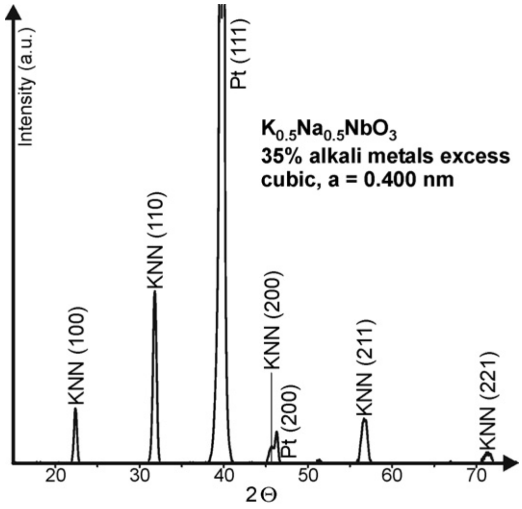

Fig. 2. Perovskite phase of KNN as obtained from thin film samples prepared with 35% alkali-metal excess. As compared to powder diffractograms of KNN, the peak intensity of the (1 1 0)-peak is higher, indicating a {1 1 0}-texture of the film.

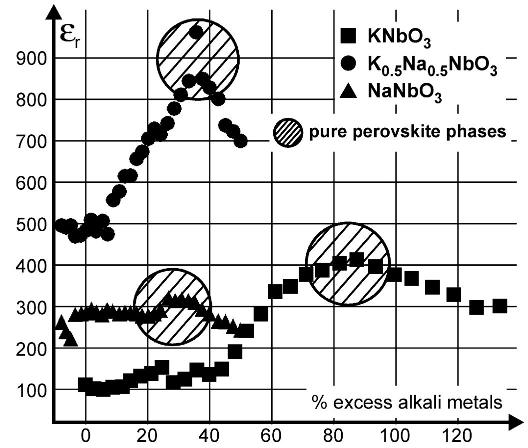

Fig. 3. Measurement of the dielectric constant of a thin film library containing KN, KNN and NN compositions with progressively varied amount of alkali-metal excess. The distinct peaks indicate samples of high phase purity.

drying of the samples at 50 °C. The leakage current measured at ambient conditions thus is supposed to be due to water absorbed in the porosity of the film. Exposed to ambient conditions, water absorption occurs within several seconds, indicating severely hygroscopic thin films. The dielectric constant experiences a drop of 5% only upon drying. Usually, at least five spots/sample were measurable.

5. Conclusion

A high throughput method was used to develop pure perovskite phase thin films of the binary $KNbO_3$–$NaNbO_3$ system on Pt substrates by CSD. Volatility of alkaline metals during processing leads to K- or Na-deficient phases, when stoichiometric precursors are used. It was possible to accurately determine the required excessive amounts of these elements to compensate for their loss. Rather than from XRD, the optimal compositions can be determined more precisely from the distinct peaks of the dielectric measurements, as small amounts of secondary phases may not be visible in a diffractogram of a thin film, yet lead to a strong decrease of the dielectric constant.

The highest values of the dielectric constant are found for the KNN composition near the MPB. As compared to pure KN, superior ferroelectric properties can be expected for this composition. Further, the Na content was found to improve film quality, as can be concluded from the lower roughness and lower dielectric loss of Na-rich compositions. The correspondence between roughness and dielectric loss gives rise to the assumption, that the loss mechanism is an extrinsic one. An improved film quality should reduce these losses, enabling a more accurate determination of the intrinsic material properties. Hysteresis measurements are under way to learn about the ferroelectric characteristics of these films.

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